Chemistry and Technology of Explosives

Vol. I

by

TADEUSZ URBANSKI

Department of Technology, Politechnika

Warszawa

Authorized translation by

IRENA JECZALIKOWA

and

SYLVIA LAVERTON

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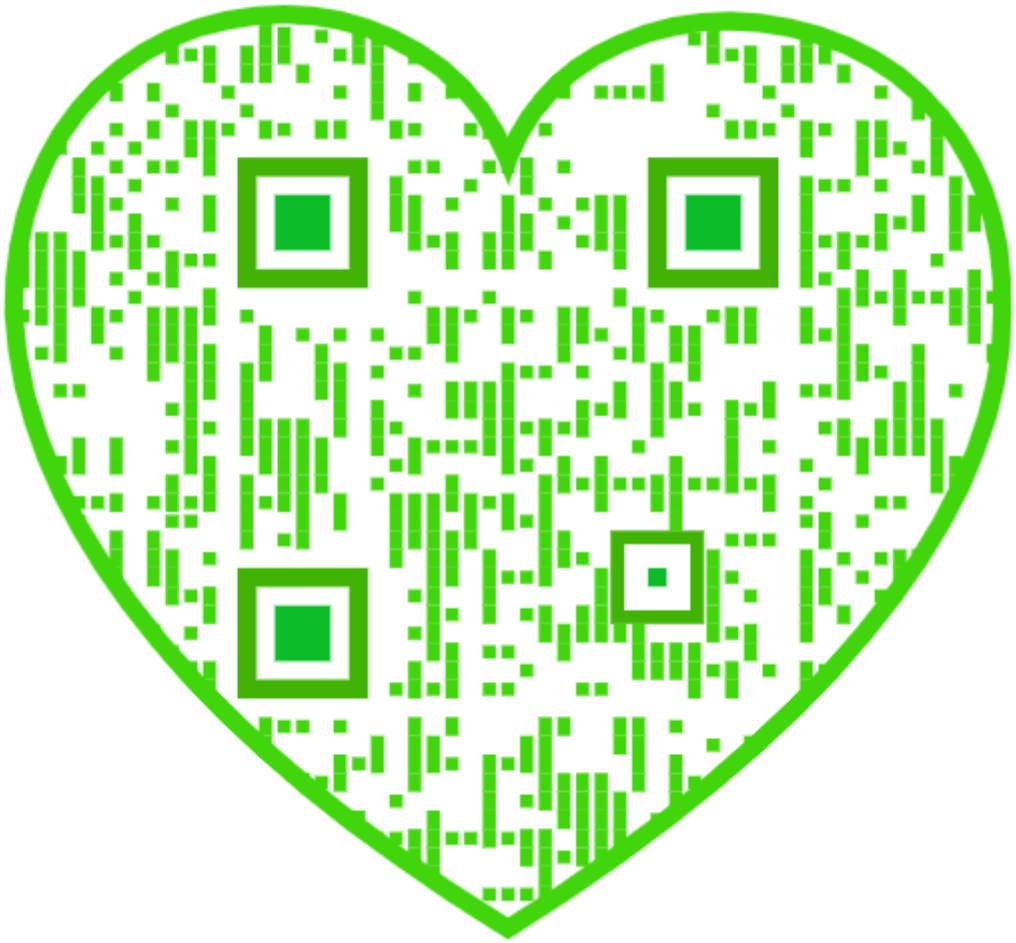

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PREFACE

For quite a long time a reference book has been needed which would provide the reader with adequate information, both theoretical and practical, on the chemistry and technology of explosives. The objectives of the present book are to fill this gap in the chemical literature.

The first edition appeared in Warsaw in Polish in 1953-54. The second, in Czech, was printed in Prague in 1958-59. The third, in German, is being printed in Leipzig. The present fourth edition is a considerably revised and expanded version of the earlier ones.

The chemical, physical and physico-chemical properties of explosives are dealt with, and processes of manufacture are described whenever the substance in question is of practical importance.

The basis of all practical knowledge is in the underlying theory. The scientist working on technological problems in industry should never forget that science, however applied, remains a natural philosophy. This is why particular attention is paid here to the chemical and physico-chemical properties of the substances described in the book, and the author has endeavoured to bring this information up to date, hoping that the wide scope of this information will not obscure the main subject, but will help, instead, to avoid narrow specialization which creates the danger of not seeing the wood for the trees.

It is also hoped that in widening the scope of the book, it might become useful not only to students and experts on explosives, but also to all who are interested in the chemistry of such substances as nitro compounds, nitramines, nitric esters, nitric salts, azides etc. that may serve as intermediates for organic reactions.

As far as processes of manufacture of explosives are concerned, information is obviously restricted, as the exact details are seldom available. However, certain obsolete methods of manufacture are described in detail. They have been included in order to give some idea of the way such processes have developed on the basis of years of experience. This may be of some value, for the manufacture of explosives is bound to be dangerous and any method, even an obsolete one, may suggest how risks can be avoided or diminished and the kinds of precaution that can be applied.

However, it has been possible to include in the book details of a number of

original processes used in the German and Japanese explosives industries during World War II which were revealed after the war mainly in CIOS, BIOS, FIAT and PB publications.

Although there was an enormous increase in the use of explosives for destructive purposes in the two World Wars it is still true to say that more explosives have been used in peace than in war. Modern civilization and modern progress would be impossible without explosives. Particular attention has therefore been paid to coal-mine explosives (Vol. III). Also a modest chapter on rocket fuels has been included in the English edition.

It is a pleasure to express my thanks to my friends for their interest in this work and their kind assistance. To all of them who helped me to bring my book up to date and to avoid mistakes so easy in so large a book, I express my warmest thanks.

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Finally I would like to express my thanks to all editors and authors who have granted their permission to reproduce the figures and diagrams reprinted from their work.

With the large field dealt with in the book, many important papers must have been overlooked and I should be grateful if readers would call my attention to any omissions so that corrections and additions could be made in the future.

T. Urbanski

Department of Organic Technology,
Politechnika

Warszawa 10,
Poland
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CLASSIFICATION OF EXPLOSIVES

EXPLOSIVES may be classified both from the chemical point of view and according to their uses. From the chemical viewpoint we distinguish between chemical individual substances and mixtures.

The former are divided into:

(1) nitro compounds
(2) nitric esters
(3) nitramines
(4) derivatives of chloric and perchloric acids
(5) azides
(6) various compounds capable of producing an explosion, for example fulminates, acetylides, nitrogen rich compounds such as tetrazene, peroxides and ozonides, etc.

Individual substances are explosive if their molecules contain groups which confer upon them explosive properties. The first attempt at a systematic approach to the relation between the explosive properties of a molecule and its structure was made by van't Hoff [l]. He pointed out, that in the molecules of explosive compounds the following groups were present:

O-O in peroxides and ozone and ozonides
O-Cl in chlorates and perchlorates
N-Cl in nitrogen chloride
N=O in nitro compounds, nitric acid esters and salts
N=N in diazo compounds, hydrazoic acid, its salts and esters
N=C in fulminates and cyanogen
CEC in acetylene and acetylides.

A further effort to establish a relationship between explosive properties and structure has been made more recently by Plets [2]. He proposed a theory of "explosophores" and "auxoploses" in a way analogous to Witt's suggested chromophores and auxochromes in the dyes, and Ehrlich's suggested toxophores and autotoxes in chemotherapeutics.

According to Plets the explosive properties of any substance depend upon the presence of definite structural groupings, called ***explosophores.*** The auxoploses fortify or modify the explosive properties conferred by the explosophore. Plets

divided all explosives into eight classes containing the following groups as explosophores:

(1) $-NO_2$ and $-ONO_2$, in both inorganic and organic substances
(2) -N=N- and -N=N=N- in inorganic and organic azides
(3) $--NX_2$, for example in NCl_3 (X- a halogen)
(4) -N=C in fulminates
(5) $-OC1O_2$ and $-OC1O_3$ in inorganic and organic chlorates and perchlorates respectively
(6) -O-O- and -O-O-O- in inorganic and organic peroxides and ozonides respectively
(7) -CEC- in acetylene and metal acetylides
(8) M-C metal bonded with carbon in some organometallic compounds.

Although this classification is in principle correct, the distinction between the terms “explosophore” and “auxoplose” is very vague and of little practical value.

A further step in the classification of explosives was made by Lothrop and Handrick [3]. They collected and classified all the available information on the performance of explosives and related it to four factors: oxygen balance, “plosophoric” groups, “auxoplosive” groups, heat of explosion.

A *plosophore* has been defined as a group of atoms which is capable of forming an explosive compound on introduction into a hydrocarbon. According to these authors there are two classes of plosophores differing sharply in effectiveness and consistency in producing power. Hence it is suggested that these be called “primary” and “secondary” plosophores.

Primary plosophores include nitrate esters, aromatic and aliphatic nitro groups and the nitramine group.

The secondary plosophores that comprise the remainder include such groups as azo, azide, nitroso, peroxide, ozonide, perchlorate, etc.

If more than one type of these groups is present such a molecule may be named a *hybrid* according to Lothrop and Handrick.

Groups which do not themselves produce explosive properties, but may influence them in the same way that auxochromic groups vary the colour intensity and shade of a dye, are called *auxoplosives* by these authors. We may quote hydroXY~, carboxyl, chlorine, sulphur, ether, oxygen, amine, etc. as examples of such groups.

* Although the classification of groups existing in explosive molecules suggested by Lothrop and Handrick may be accepted, their far-reaching postulations concerning a close relation between the oxygen balance and performance of explosives aroused strong criticism [4]. It is known that the oxygen present, for example, in carbonyl or hydroxyl groups, has little effect on the performance of an explosive. This is due to the high heat of formation of C-O and C-O-H bonds. On the contrary, the low (negative) heats of formation of N--O and CEC bonds are of great significance in relation to the performance of explosives.

That is the reason why the performance of picric acid (trinitrophenol) is only vary slightly higher than that of trinitrobenzene and why the performance of trinitroanisole is much the same as that of trinitrotoluene.

The low value of the explosive power of oxygen atoms bonded with carbon and hydrogen atoms in such a group as COOH had already been stressed by Stettbather [5], who also pointed out that an exception is provided by peroxides and ozonides which form exothermic bonds that considerably enhance explosive performance-

However, the slightly better performance of picric acid compared with trinitrobenzene is probably the result of the former's greater ability to detonate. The ease of detonation of picric and styphnic acids as compared with trinitrobenzene is well known. D. Smolenski and Czuba [6] recently pointed out that dinitrophenol detonates more readily than dinitrobenzene.

It is also well known from the classic work of L. Wöhler and Wenzelberg [7] that the sensitivity to impact of aromatic nitro compounds increases with increase in the number of substituents for a given member of the nitro groups.

Explosive mixtures can be divided into:

(1) those with at least one explosive component

(2) others where there is no explosive component.

The classification of mixtures will be dealt with in detail in Vol. III.

According to their uses explosives are divided into high explosives, propellants ('low explosives") and primary explosives or initiators.

High explosives may be class&d according to their physical properties as powdery, meltable, semi-meltable and plastic. Propellants may be grouped on the basis of chemical composition into gun powder and similar mixtures, nitrocellulose (single base) and nitroglycerine (double base) powders. With respect to their uses and some properties they are divided into black powder, smokeless and flashless powders, and rocket propellants.

Primary explosives and their mixtures are divided into those used for filling ignition caps and those used in detonators.

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CHAPTER I

NITRATION AND NITRATING AGENTS

GENERAL INFORMATION

NITRATION is one of the earliest known organic chemical reactions. It is mentioned in the writings of the alchemists. As early as in the first half of the XVIIIth century Glauber obtained picric acid by acting on wool and horn with nitric acid. Soon reactions between nitric acid and a variety of organic substances became one of the alchemical reactions most frequently used. They were usually carried out by heating a substance with nitric acid, often to boiling point. Thus picric acid was obtained from certain organic substances such as indigo, silk, resins, etc.

In 1833 Braconnot obtained nitric esters of cellulose and starch by acting with nitric acid on plant fibres and starch, at low temperature. In 1834 Mitscherlich nitrated benzene to nitrobenzene. But it is only since 1842, when Zinin reduced nitrobenzene to aniline, that rapid development of the chemistry of nitro compounds and their application to organic industry has occurred.

At present nitration is one of the most widely applied direct substitution reactions. This is due to several factors. For example nitration usually proceeds easily, its products can readily be separated from the spent acid, and there is a wide range of possibilities in the practical use of nitro compounds, both as intermediates and end products. The presence of a nitro group in the starting product made it possible to obtain a number of basic organic intermediates such as aniline and benzidine. Dyes with more than one nitro group, such as picric acid were obtained. It has been found that higher nitrated nitro compounds and nitric acid esters have explosive properties and are of practical importance. Some nitro compounds are used in perfumes. Medicinal properties have lately been discovered in certain nitro compounds, e.g. chloramphenicol.

Nitration is a reaction which has contributed greatly to the development of the substitution rule [I]. Although nitration had been well known and widely used for many years both in the laboratory and in industry, little was known about the nature and mechanism of this reaction until recently. However, in the last two decades much progress has been made in this field.

With the aid of the new techniques offered by modem physics and physical chemistry and by the application of the modem electronic theory of chemical bonds,

certain difficult problems have been elucidated in the course of extensive research so that now what might be defined as a modern theory of nitration can be outlined, although it is still far from being perfect.

Nitration can be carried out either directly by introduction of the nitro group in place of hydrogen atom or by adding it to a double bond, or else indirectly, by introducing into a compound a group which can readily be substituted by the nitro group.

The following nitrating agents are most frequently used for the direct introduction of the nitro group:

(1) concentrated nitric acid

(2) mixtures of concentrated nitric acid and concentrated sulphuric acid (or oleum) in different proportions-these are usually known as nitrating mixtures

(3) alkali nitrates in the presence of sulphuric acid

(4) dilute nitric acid

(5) nitrogen dioxide

(6) a solution of nitrogen dioxide in sulphuric acid

(7) nitrogen dioxide in the presence of catalysts.

For laboratory experiments and sometimes in industry more expensive nitrating agents may be used, as for example solutions of nitric acid in inert organic solvents (chloroform, carbon tetrachloride, ether, nitromethane, etc.), or a solution of nitric acid in phosphoric or acetic acids or in acetic anhydride. The use of these nitrating agents may be of some practical value and will be discussed later on in detail.

For nitrating on the laboratory scale, mixtures of nitric acid esters or acyl nitrates, e.g. acetyl nitrate CH_3CONO_3, and sulphuric acid may also be used.

Several lesser known nitrating agents, which can find practical use on a laboratory scale are metal nitrates in the presence of acetic acid or acetic anhydride, described by Menke [2], tetranitromethane and hexanitroethane in an alkaline medium, used by Schmidt [3], and nitroguanidine in solution in sulphuric acid, used for the nitration of aromatic amines and phenols.

Besides these direct methods of introducing nitro groups, several indirect methods are known that consist in the introduction of a group which can readily be substituted by a nitro group. In one of these which is widely used in the nitration of phenols, a compound is sulphonated and subsequently, by reaction with nitric acid, the sulpho group is replaced by the nitro group.

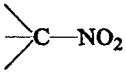
Other indirect nitration methods applied on an industrial scale, for nitrating phenols, comprise: introducing a nitroso groups into the phenol and then oxidizing it to the nitro group, and a method involving oxidation of a primary amino group to the nitro group.

In experimental work indirect methods of introducing nitro groups find wide application as, for example, the substitution of a halogen (iodine or bromine in an alkyl iodide or bromide) by the Nitro group, by means of silver nitrite (the Victor Meyer reaction), and the new modification of this method described recently by Kornblum et al. [4, 4a], in which alkyl halides are reacted with sodium nitrite.

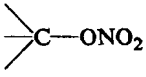
In aromatic compounds, an amino group may be substituted by the nitro group by diazotization and reacting with nitric acid in the presence of cuprous salts (the Sandmeyer reaction). This method is used for laboratory work only and is described in textbooks on preparative organic chemistry.

With respect to the chemical structure of compounds resulting from nitration processes, three types of nitration reactions are distinguished which may be referred to as:

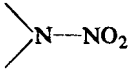
(1) C-nitration, leading to the formation of "true" nitro compounds, having the nitro group attached to a carbon atom:



(2) O-nitration, leading to the formation of nitric acid esters, with the nitro group attached to an oxygen atom:



(3) N-nitration, leading to the formation of nitramines with the nitro group attached to a nitrogen atom of an amine or amide group:



NITRIC ACID

The physical constants of chemically pure nitric acid are

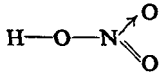
specific gravity	1.51
specific heat	0.5 k&/kg
melting point	-41.6°C
boiling point	+86°C
heat of formation	-41.66 kcal/mole

At the boiling point nitric acid undergoes partial decomposition which proceeds chiefly according to the equation:

$$2HNO_3 \rightarrow 2NO_2 + H_2O + \tfrac{1}{2}O_2 \qquad (1)$$

At higher temperatures the degree of decomposition is greater and at 256°C it is complete.

In conformity with the accepted notation for simplified electronic formulae, the structural formula of nitric acid according to Sugden is



As this formula indicates in the nitro group one atom of oxygen is linked to the nitrogen atom by a double bond, the other-by a semipolar linkage (see Chapter V on the structure of the nitro group, p. 168). Bond distances and bond angles have been calculated by Maxwell and Mosley [5] (Fig. 1a), using their own experiments

on the electron diffraction of nitric acid vapour and measurements of the Raman spectrum of anhydrous nitric acid by Chedin [6].

Nitric acid molecules are linked by hydrogen bonds. This assumption was based originally on the results of studies of the nitric acid absorption spectrum in the very near infra-red (ca. 1μ) by Badger and Bauer [7], Dalmon [8], Dalmon and Freymann [9] and also on the X-ray investigation by Luzzati [10] (Fig. 16).

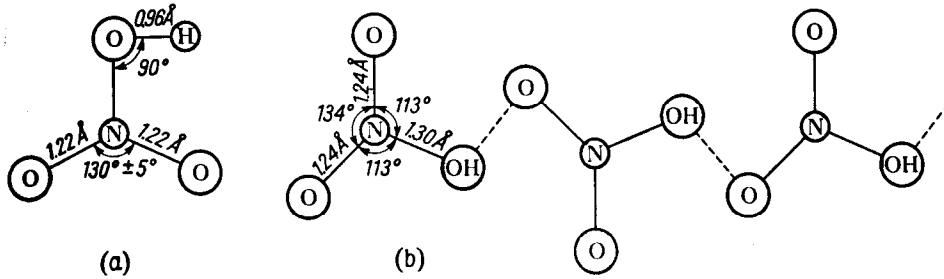
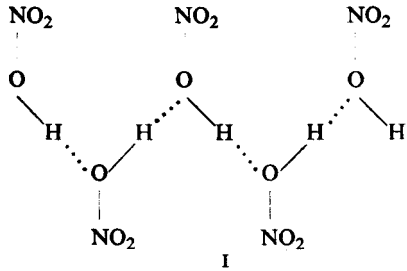


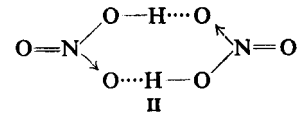
FIG. 1. (a) Bond distances and bond angles of the molecule of nitric acid (Maxwell and Mosley [5]); (b) Crystalline nitric acid: molecules of nitric acid associated through hydrogen bonds (Luzzati [10]).

More recent infra-red investigations have confirmed the existence of hydrogen bonds. According to Ingold, Cohn and Poole [40] they exist even in the vapour phase.

The association of the molecules is presented by a chain (I) or a ring (II) formula. In both cases hydrogen bonds are present between the OH and NO_2 groups.

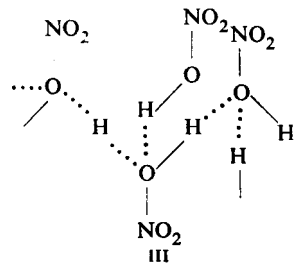


I



II

Gillespie and Millen [11] suggested another form of presentation of the association of nitric acid molecules by means of hydrogen bonds. They assumed that oxygen atoms linked by hydrogen bonds are tetrahedrally coordinated as in water molecules (III) :



III

They believe that this formula is better than the others in explaining the ability of nitric acid to dissociate. Moreover it is consistent with the low basicity of the nitro groups (which is discussed later, see p. 218).

A more detailed review of research work on the absorption spectra of nitric acid is given later (see p. 19-27).

Nitric acid forms hydrates with water: $HNO_3 \cdot H_2O$ (m. p. -38°C) and $HNO_3.3H_2O$ (m. p. -18.5°C). The chief evidence for these hydrates is obtained from the thermal analysis of the system nitric acid-water (Fig. 2). Other experimental

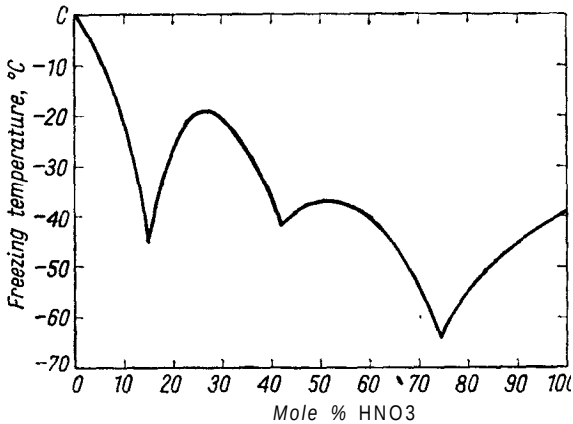


FIG. 2. Thermal analysis of nitric acid-water system.

facts also confirm the existence of addition compounds of nitric acid and water. Thus the *refractive* ***index*** shows, according to Veley and Manley [12], a linear relation over the range from 78 to 91% concentration. At 91% a sharp inflection occurs, and above 98.5% the slope of the curve is reversed. The ***electrical conductivity*** also shows anomalies over this concentration range, passing through a minimum.

The considerable heat evolved on dilution of nitric acid with water proves that the nitric acid hydrates are stable. With an excess of nitric acid the heat amounts to 3.5 kcal per mole of water. It has been suggested that the nitric acid hydrate, $HNO_3.H_2O$, present in concentrated nitric acid is undissociated and that the water molecules are attached to the nitric acid molecules by hydrogen bonds. Thus there would be the equilibrium :

$$NO_2{-}O \quad H\cdots O\begin{matrix}H\\H\end{matrix} \rightleftharpoons NO_3^{\ominus} + H_3O^{\oplus} \qquad (2)$$

Nitric acid acts on organic compounds both as a nitrating and as an oxidizing agent. The reaction depends on the compound being nitrated and on the concentration of the nitric acid. In accordance with a general rule, a concentrated nitric acid acts mostly as a nitrating agent. When diluted its nitrating action diminishes

accordingly and finally gives way to an oxidizing action. The more dilute the nitric acid the more vigorous (up to a limit) is the oxidizing action. Extensive research into the physical properties of nitric acid, especially that which has been carried out recently, has been aimed at finding an explanation of this double function of nitric acid.

The limiting concentration of the nitric acid in a nitration process depends largely on the nitrated compound itself. Some phenols, for example, can be nitrated with nitric acid in concentrations of below 5%, while benzene does not nitrate at those concentrations. Aliphatic hydrocarbons can be nitrated even with 13 % nitric acid.

Knowing how a nitration process is likely to proceed is possible only when the structure of the nitrating agent itself is known. This is why a great deal of research work has been devoted lately to the elucidation of the structure of nitric acid when pure and in mixtures with other mineral acids.

The most frequently used nitrating mixture is the one comprising nitric plus sulphuric acids. The role of the sulphuric acid has been the subject of many investigations. These are described in the following section.

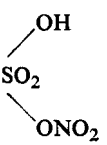
The most recent review of the physicochemical properties of nitric acid is that of Stern, Mullhaupt and Kay published in 1960 [12a].

NITRIC ACID IN ADMIXTURE WITH OTHER MINERAL ACIDS

EARLIER WORKS

Muspratt and A. W. Hofmann [13] were the first to use a mixture of nitric and sulphuric acids for nitrating nitrobenzene to dinitrobenzene.

Initially sulphuric acid was considered to act as a “dehydrating agent” in a nitrating mixture with nitric acid. This view was expressed in the literature for the first time by Spindler [14]. The first attempt to elucidate the form of nitric acid in admixture with sulphuric acid was a hypothesis formulated by Markovnikov [15]. It assumed that the two acids form a mixed anhydride, i.e. nitrosulphuric acid :



Later Sapozhnikov [16] developed a theory, based on density, electrical conductivity and partial vapour pressure measurements. He assumed a state of equilibrium between the hydrates of the two acids in their mixtures:

$$HNO_3 \cdot nH_2O + xH_2SO_4 \longleftrightarrow HNO_3 \cdot (n\text{-}x)H_2O + xH_2SO_4 \cdot H_2O \qquad (3)$$

Since the affinity of water for sulphuric acid is higher than that for nitric acid,

nitric acid gradually becomes dehydrated with increase in concentration of sulphuric acid. Finally, at x = n, nitric acid becomes anhydrous.

$$HNO_3 \cdot nH_2O + nH_2SO_4 + HNO_3 + nH_2SO_4 \cdot H_2O \quad (4)$$

At high concentrations (mixtures with a low water content) Sapozhnikov found certain anomalies in the vapour pressure of HNO_3 and in its electric conductivity. He ascribed them to the formation of nitric anhydride N_2O_5. Thus the equation will be:

$$2HNO_3 + H_2SO_4 \rightarrow N_2O_5 + H_2SO_4 \cdot H_2O \quad (5)$$

Later, to confirm his theory, Sapozhnikov gave some data on the O-nitration of cellulose with nitric acid (see Vol. II) and on the nitration of naphthalene (p. 427).

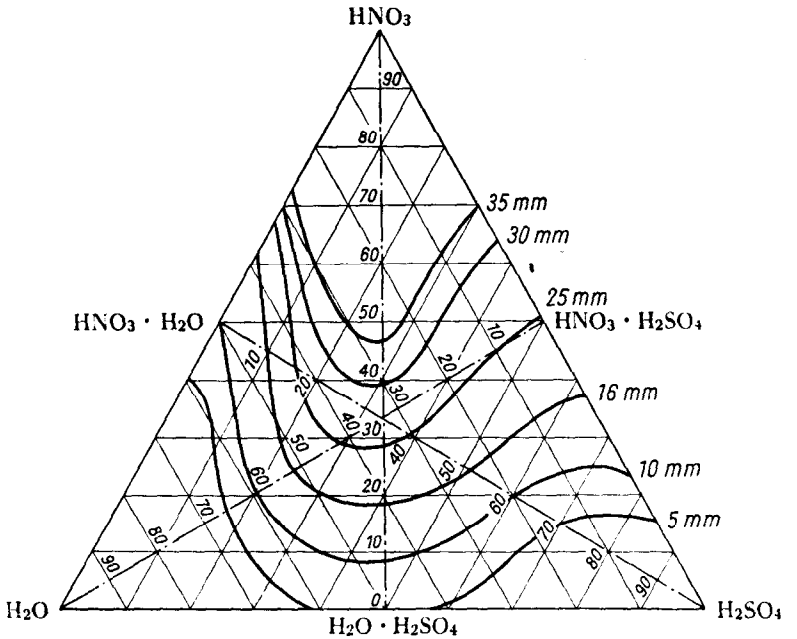


FIG.. 3. Isobars of partial vapour pressure of nitric acid in nitric acid-sulphuric acid-water mixtures (Sapozhnikov [16]).

The nitration curves for these compounds when nitrated with nitrating mixtures are similar to the vapour pressure curves of nitric acid in mixtures, presented after Sapozhnikov in Fig. 3.

Sapozhnikov's view was partly confirmed by Walden [17]. Halban and Eisenbrand found [18] that the absorption spectrum of pure nitric acid in the ultraviolet differed completely from its spectrum when in solution in anhydrous sulphuric acid. The authors explained this observation by assuming the existence of the nitric anhydride or the mixed nitric-sulphuric anhydride. This assumption seemed to be all the more probable as in some earlier papers the idea had already been expressed that N_2O_5 might exist in concentrated nitric acid. Thus in 1898

veley and Manley [12] suggested it on the basis of the existence of an electric conductivity minimum at a nitric acid concentration of 96-97% HNO_3 and later, in 1903, the same authors found evidence in refraction coefficient measurements, then Küster and Münch [19] in 1905, published further evidence based on measurements of the properties of the anhydrous nitric acid.

In his later studies Hantzsch assumed, according to the Brönsted theory of acids and bases, that nitric acid acts as a base towards sulphuric acid. According to Brõnsted, an acid is a compound able to give off a proton while a base is a compound able to take up a proton.

The acidic character of a compound At appears in the presence of another compound B_1, which itself behaves like a base:

$$A_1 \rightarrow B_1 + H^+$$

As a free proton cannot exist it must be attached to a base B_2. As a result, an acid A_2 is formed:

$$H^+ + B_2 \rightarrow A_2$$

The two reactions sum up to give a new one:

$$A_1 + B_2 \leftrightarrow A_2 + B_1$$

in which the proton is transferred from an acid A_1 or A_2 to a base B_2 or B_1.

One of the components of the system may be a solvent. This is the case, for example, with a solution of nitric acid in sulphuric acid. The sulphuric acid, with a very small affinity for the proton, plays the role of an acid and nitric acid behaves like a base.

Usanovich [20] and Lewis [20a] have generalized the Brõnsted theory. The latter considered adds to be compounds which are able to employ a lone pair of electrons from another molecule; bases are compounds having a lone pair of electrons which may be used by another molecule.

Hantzsch opposed the theory of N_2O_5 existing in the nitrating mixture HNO_3 + + H_2SO_4 Due to the importance of the Hantzsch theory in the development of our views on the nature of the nitration process, we shall discuss it in detail. In a number of works Hantzsch [21-23] developed a theory based on Schäfer's experiments [24] on the absorption spectrum in ultra-violet light. Schäfer's chief observation was, that the spectrum of anhydrous nitric acid in a non-aqueous solvent (hexane, sulphuric acid, etc.) is analogous with the spectra of nitric acid esters.

On the basis of these data Hantzsch assumed that, generally speaking, acids have two forms:

(1) true acids with a spectrum similar to that of metal salts

(2) pseudo-acids with a spectrum similar to that of esters.

According to Hantzsch, the structure of a true nitric acid is $NO_3^-H^+$ or $N(O_3)^-H^+$. The hydrogen atom is attached by electrostatic force only and that is why it dissociates readily, while the structure of concentrated nitric acid is that of the undissociated pseudo-acid NO_2.OH or $N(O_2)OH$.

Both forms are in equilibrium. The pseudo-acid form acts as a nitrating and

esterifying agent. The addition of water shifts the equilibrium towards the formation of the dissociated form of the true acid, which has no nitrating properties:

$$NO_2.OH \overset{H_2O}{<->} NO_3^-H^+ \quad (6)$$

Thus, the addition of sulphuric acid to nitric acid increases the concentration of the pseudo-acid. The sulphuric acid, being the stronger, gives off a proton to pseudo-nitric acid and causes the formation of the following mono- and bivalent ions :

$$NO_2.OH + H_2SO_4 \rightarrow NO(OH)_2^+ + HSO_4^- \quad (7)$$

$$NO_2.OH + 2H_2SO_4 \rightarrow N(OH)_3^{2+} + 2HSO_4^- \quad (8)$$

Hantzsch named the ion $H_2NO_3^+$ *nitracidium*, and the ion $H_2NO_3^{2+}$ *hydronitrucidium*. In particular, the eqn. (8), according to which the $H_3NO_3^{2+}$ ion is formed, appeared to be correct in the light of Hantzsch's cryometric studies [21] published in 1909. He found that the freezing point of sulphuric acid fell very considerably when nitric acid was added, indicating that the value of the van't Hoff i-factor (in the equation PV = ***inRT)*** ranges from 3.4 to 4.0. Among other cryometric investigations, measurements by Oddo and Scandola [25], Hammett, et al. [26-28], Robles and Moles [29] should be mentioned. On the whole they are in agreement with Hantzsch's data.

To obtain further arguments for the confirmation of his theory in 1925 Hantzsch [21] examined the ultra-violet absorption spectra of nitric acid. On dilution with water a band appears which may be ascribed to the NO_3^- ion. The band is not present in solutions of nitric acid in sulphuric acid, since, as the author says, the ions $H_2NO_3^+$ and $H_3NO_3^{2+}$ must appear in such circumstances.

Halban [18] reported, in the paper already referred to, that the difference between the absorption spectrum of pure nitric acid and that of its mixture with sulphuric acid is due to the presence of N_2O_5 in the mixture, while Walden [17] believed instead that it was the ***nitronium ion,*** NO_2^+, which will be discussed later, that was present in the mixture.

Hantzsch tried to obtain further evidence for the existence of the above mentioned ions, using the electric conductivity method but without success. Finally he tried to isolate the sulphates of the two hypothetical ions nitracidium and hydronitracidium:

$$(H_2NO_3)^+(HSO_4)^- \text{ and } (H_3NO_3)^{2+}\ (HSO_4)^{2-}$$

Although he did not succeed in isolating these salts he postulated, for confirmation of his theory, that the compound with the empirical formula $N_2O_5.4SO_4.3H_2O$ isolated by Weber as early as in 1871 is a salt of pyrosulphuric acid :

$$(H_2NO_3)^+\ (HS_2O_7)^- \text{ or } (H_3NO_3)^{2+}(S_2O_7)^{2-}$$

An observation by Holmes [30] seemed to confirm Hantzsch's hypothesis; Holmes demonstrated by thermal analysis the existence of the molecular compound

$(H_2SO_4)_5.HNO_3$ or N_2O_5. 10 SO_3. 11 H_2O with a melting point of +23°C. In 1949 Dade [31] demonstrated in the same way the existence of the compound $2N_2O_5$. $.11SO_3.9H_2O$ (m. p. +18.8°C) and Heertjes and Revallier [31a] the existence of the compound $HNO_3.2SO_3$, which according to Spasokukotskii [59] is nitronium pyrosulphate $NO_2^+.HS_2O_7^-$.

At last in papers published between 1925 and 1928, Hantzsch referred to the analogy between above-mentioned compounds and those of nitric and perchloric acids [21-23]. He reported that he had succeeded in isolating crystalline nitracidium and hydronitracidium perchlorates :

$$(H_2NO_3)^+(C1O_4)^- \quad \text{and} \quad (H_3NO_3)^{2+}(C1O_4)^{2-}$$

According to Hantzsch nitracidium and hydronitracidium nitrates are present in concentrated nitric acid:

$$(H_2NO_3)^+(NO_3)^- \quad \text{and} \quad (H_3NO_3)^2+(NO_3)_2^-$$

The Hantzsch theory was supported by Lauer and Oda [32], who examined the nitration of anthraquinone and nitrobenzene with mixtures of nitric and sulphuric acid, the sulphuric acid containing from 20% water to 5% sulphur trioxide.

They found that the activation energy of the nitration reaction was 21.65 kcal/mole when the water content of the sulphuric acid was in the range 4.4-13%, while it was only 13.30 kcal/mole when anhydrous sulphuric acid was present. The reaction rate was higher in the presence of these concentrations of water than in the non-aqueous medium. Hence Lauer and Oda came to the following conclusions:

1. In a mixture with 89% sulphuric acid, nitric acid exists in two forms -true nitric acid and pseudo-nitric acid, according to Hantzsch's theory. Only the pseudo-acid form acts as a nitrating agent. On dilution with water the concentration of pseudo-acid falls.

2. In mixtures with 89-98% sulphuric acid, nitric acid exists principally as pseudo-nitric acid with a certain quantity of sulphate of nitric acid also present.

3. When 98-100% sulphuric acid is used, the nitric sulphate content increases.

4. In a non-aqueous mixture containing free SO_3 it is only the nitric sulphate which acts as a nitrating agent.

A quite different hypothesis was suggested by Euler [33] in 1903. He assumed that a solution of nitric acid in sulphuric acid contains the nitronium or nitryl ion, NO_2^+. Subsequently in 1922 he confirmed this hypothesis.

This view was supported later by Walden [17]. Considering the high electrical conductivity of nitric acid he believed that HNO_3 should be regarded as an amphoteric electrolyte, an idea expressed by the equilibrium equation:

$$HNO_3 \text{ <-> } H^+ + NO_3^- \text{ <-> } OH^- + NO_2^+ \qquad (9)$$

On the basis of conductometric studies and taking into account the catalytic action of nitrogen dioxide in the nitration Klemenc and Schöller [34] suggested

that a hypothetical "E-acid" is formed in the reaction of nitric acid with nitrogen dioxide and is the entity responsible for nitration:

$$2HNO_3 + NO_2 \leftrightarrow \underset{\text{E-acid}}{H_2N_3O_8} \quad (10)$$

According to those authors the nitration reaction occurs as follows:

$$2RH + H_2N_3O_8 \rightarrow 2RNO_2 + NO_2 + H_2O \quad (11)$$

There was no doubt at that stage of the investigation that nitric acid reacts with sulphuric acid. Yet the research work described had put forward a problem without giving a clear answer. It was only in recent investigations that, due to more accurate physico-chemical methods, especially to the application of Raman spectrum analysis, inferences about the interaction of the nitrating mixture components have been confirmed.

MORE RECENT STUDIES

Cryometric investigations

Hantzsch's work and his conclusions have lately been revised and criticized. In his extensive work published in 1941, Titov [35] drew attention to the fact that none of the existing view about the action of sulphuric acid on nitric acid explained Hantzsch's observation that the value of the van't Hoff i-factor for nitric acid dissolved in sulphuric acid may be close to 4.

Titov quotes the following equations, based on different existing views:

$$HNO_3 + 2H_2SO_4 + (HO_3S)ONO_2 + H_2SO_4.H_2O \quad (12)$$

(equation based on Markovnikov's view)

$$2HNO_3 + H_2SO_4 + N_2O_5 + HSO_4^- + H_3O^+ \quad (13)$$

(equation based on Sapozhnikov's view) and Hantzsch's eqns. (7) and (8) quoted earlier.

According to Titov, the simplest way of explaining Hantzsch's observations is in the form of an equilibrium equation, in which the nitronium cation* occurs:

$$HNO_3 + 2H_2SO_4 \leftrightarrow NO_2^+ + 2HSO_4^- + H_3O^+ \quad (14)$$

Titov believed that Hantzsch's nitracidium and hydronitracidium ions should be considered as the hydrated nitronium ions:

$$H_2NO_3^+ + H^+ \rightarrow NO_2^+ + H_3O^+ \quad (15)$$

$$H_3NO_3^{2+} \rightarrow NO_2^+ + H_3O^+ \quad (16)$$

This view was confirmed experimentally when in 1950 Ingold [36] and his co-workers isolated crystalline nitronium salts (p. 19).

* Nitronium ion is sometimes called nitryl or (more correctly) nitroxyl ion (see p. 13).

Using more precise methods of cryometric measurements Ingold [37] and co-workers had already found in 1946 that the value of van't Hoff i-factor for HNO_3 in sulphuric acid is 4.4. Ingold explained this by eqn. (18).

It should be pointed out that a similar equation for a solution of nitrous acid in sulphuric acid was suggested by Hantzsch as early as in 1909, and confirmed in his further publications of 1930-37:

$$HONO + 2H_2SO_4 <-> NO^+ 2HSO_4^- + H_3O^+ \quad (17)$$

(with the nitrosonium cation, NO^+).

The value of ***i*** can be explained by an equation assuming the formation of the nitronium ion, NO_2^+:

$$HNO_3 + 2H_2SO_4 -> NO_2^+ + 2HSO_4^- + H_3O^+ \quad (18)$$

Similarly for solutions of N_2O_5 or N_2O_4 in sulphuric acid, Ingold [38-40] and his co-workers found ***i*** = 6, which would correspond to the equations:

$$N_2O_5 + 3H_2SO_4 -> 2NO_2^+ + H_3O^+ + 3HSO_4^- \quad (19)$$

$$N_2O_4 + 3H_2SO_4 -> NO_2^+ + H_3O^+ + 3HSO_4^- \quad (20)$$

These equations have been confirmed by an examination of the nitrating properties of such mixtures.

Titov [35] also expressed the opinion that nitric acid esters in sulphuric acid yield nitronium ions, for example in the reaction with ethyl nitrate:

$$C_2H_5ONO_2 + 2H_2SO_4 -> NO_2^+ + C_2H_5OH_2^+ + 2HSO_4^- \quad (21)$$

The basic argument of Titov concerning the existence of the nitronium ion in such solutions seems to be right, especially in view of the cryometric investigations of L. P. Kuhn [41], who found that for a solution of ethyl nitrate in sulphuric acid, i = 6. This would correspond to the equation:

$$C_2H_5ONO_2 + 3H_2SO_4 -> NO_2^+ + 2HSO_4^- + H_3O^+ + C_2H_5O.SO_3H \quad (22)$$

The similarity between the ultra-violet absorption spectrum of nitric acid and that of ethyl nitrate in sulphuric acid confirms this conception.

Gillespie and Graham [42] have carried out a cryometric examination of solutions of nitric acid in oleum. The results obtained are in agreement with the following equation, postulating formation of the nitronium ion:

$$HNO_3 + 2H_2S_2O_7 -> NO_2^+ + HS_2O_7^- + 2H_2SO_4 \quad (23)$$

According to Titov's paper of 1941 nitric anhydride dissociates into the nitronium and nitrate ions:

$$N_2O_5 -> NO_2^+ + NO_3^- \quad (24)$$

Cryometric investigations carried out by Gillespie, Hughes and Ingold [42a] confirm this equation. The authors examined the system $nN_2O_5 + H_2O$, where n> 1. According to their studies, anhydrous nitric acid, present in this system, undergoes a self-dissociation in the following way:

$$3HNO_3 \rightarrow NO_3^- + NO_2^+ + HNO_3.H_2O \quad (25)$$

Calculations have shown, that the NO_2^+ and NO_3^- ions content in anhydrous nitric acid at -40°C is 1.2 and 1.7% by weight respectively. The content of water is 0.5% (in form of the nitric acid hydrate).

Bennett and his co-workers [43] confirmed this interpretation of the cryometric investigations. To prove definitely the existence of the NO_2^+ ion, they attempted to show that when electrolysed, the ion is transported towards the cathode. They did not succeed in obtaining full evidence for this, although they found that nitric acid moves away from the anode. It was only when the electrolysis was carried out in the presence of oleum and barium salts, that the transport of nitric acid towards the cathode was confirmed. Studying the cathodic polarization of nitric acid Mint [44] observed the evolution of nitrogen dioxide at the cathode. This may be an additional piece of evidence for the transport of an ion containing nitrogen (probably NO_2^+) towards the cathode.

Brand [45] gave a very simple method for the analysis of nitrating mixtures confirming the theory of the formation of the nitronium ion in solutions of nitric acid in oleum. It is well known that free SO_3 present in a solution may be titrated with water until fuming disappears. This method gives fairly accurate results. The volume of water added for the titration of a mixture HNO_3 + oleum is smaller than the quantity used for the titration of pure oleum without HNO_3. This would be evidence of the reactions:

$$HONO_2 + NO_2^+ + OH^- \quad (26)$$

$$OH^- + H^+ \rightarrow H_2O \quad (27)$$

The volume of water added in the titration of SO_3 is smaller by this amount.

Brand has shown that in a solution of nitric acid in sulphuric acid, the formation of water and the HSO_4^- ion occurs, which combine with free SO_3. The amount of the SO_3 bound corresponds to the equation:

$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+ \quad (18)$$

However, it is not only sulphuric acid added to nitric acid that increases the latter's nitrating properties, Such substances as boron fluoride (R. J. Thomas et al. [46]) or hydrogen fluoride (Simons ***et al.*** [47]) when added to nitric acid have a similar effect.

These phenomena can be accounted for by assuming formation of the nitronium ion according to the equations:

$$BF_3 + HNO_3 \rightarrow NO_2^+ + BF_3OH^- \quad (28)$$

$$2HF + HNO_3 \rightarrow NO_2^+ + H_3O^+ + 2F^- \quad (29)$$

Conductometric studies

Further conductometric studies of nitric acid by Médard [48] and later Dalmon [49] have shown that on adding water to the anhydrous acid, conductivity falls

to a minimum at concentrations of 96-97% HNO_3, and then on further dilution it rises again.

This is explained by the fact that anhydrous nitric acid is dissociated, but in the presence of small quantities of water is converted into an undissociated hydrate $HNO_3.H_2O$. It is only on further dilution that the hydrate dissociates.

In conductometric measurements of two-component system where HNO_3 was one of the components, Usanovich and his co-workers [50-50c] confirmed the view that nitric acid has an amphoteric character-it can be an acid or a base depending on the other component. Thus, it acts as a base towards sulphuric acid and as a strong acid towards water. It also acts as an acid towards CH_3OOH and CCl_3COOH and combines with these compounds, but behaves as a base with $CH_2ClCOOH$ and $CHCl_2COOH$.

Addition of compounds such as H_2SO_4, H_3PO_4, towards which nitric acid acts as a base, increases the nitrating properties of HNO_3. On the contrary, the addition of compounds such as water or nitrobenzene, towards which nitric acid behaves as an acid, decreases the nitrating action of HNO_3.

Hantzsch's argument, that with strong acids like sulphuric or phosphoric, the ions $H_2NO_3^+$ and $H_3NO_3^{2+}$ are formed, led Usanovich to the inference that it was just these cations that were the nitrating agents for aromatic compounds. On the other hand, the addition of water results in the formation of NO_3^- ions, which therefore seem to be the nitrating agents for aliphatic hydrocarbons. Swinarski and Dembiriski [51] and Swinarski and Piotrowski [52] have examined the electrical conductivity of nitric and sulphuric acid mixtures with and without water. The results of these measurements are shown in the diagram, presenting the relationship between conductivity and HNO_3 concentrations.

The principal conclusions drawn by the authors are:

1. The high conductivity of anhydrous H_2SO_4 is probably due to dissociation

$$2H_2SO_4 \leftrightarrow H_3SO_4^+ + HSO_4^- \qquad (30)$$

2. A sharp increase in the conductivity of the mixture, on adding water in quantities below 9% H_2O, indicates the complete ionization of nitric acid. Probably the dissociation may be expressed by eqn. (18) which has already been referred to

$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+ \qquad (18)$$

3. The conductivity diminishes with further increase in concentration of HNO_3. The reason for this may be the formation of less mobile ions, for example Hantzsch's hydrated nitronium ion:

$$HNO_3 + 2H_2SO_4 \rightarrow H_3NO_3^{2+} + 2HSO_4^- \qquad (31)$$

The authors pointed out the similarity of the conductivity curves (Fig. 4) and viscosity curves (Fig. 14) which they observed. The shapes of both curves may be explained in the same way, namely by the formation and disappearance of $(H_3NO_3)^{2+}$ and NO_2^+ ions.

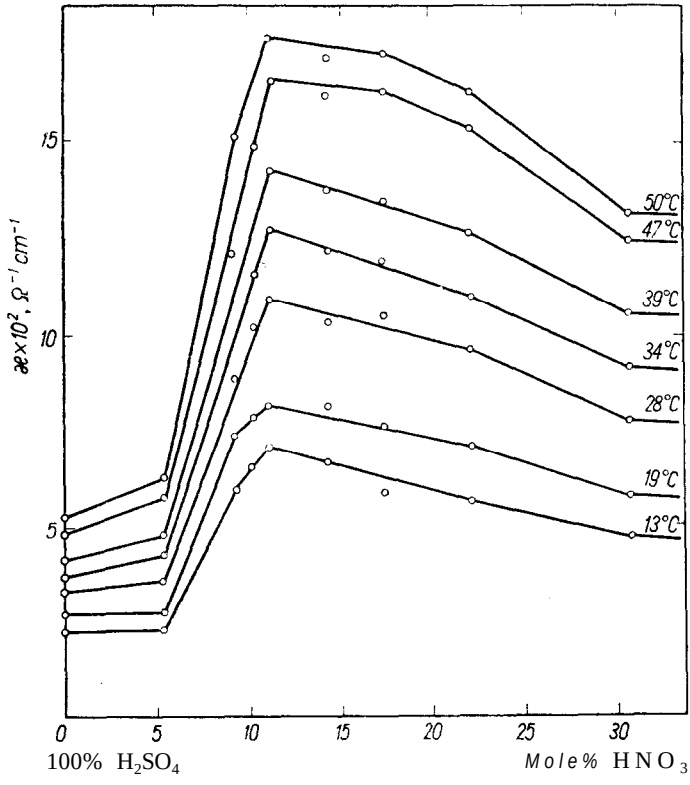


FIG. 4. Conductivity of nitrating mixtures at various temperatures (Swinarski and Piotrowski [52]).

Swinarski and Piotrowski also examined the conductivity of pure nitric and sulphuric acids as a function of temperature (Fig. 5). The curve for nitric acid has a maximum at 20°C. At 40°C the conductivity falls.

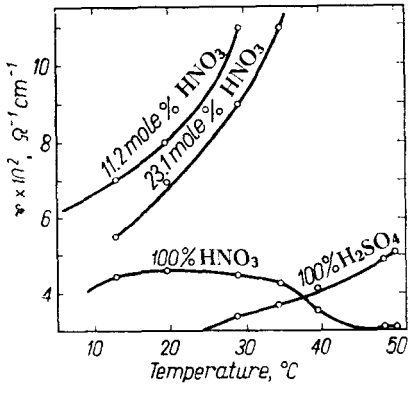


FIG. 5; Conductivity of nitric and sulphuric acid at various temperatures (Swinarski and Piotrowski [52]).

Two phenomena seem to be superposed. One is the normal increase of conductivity with temperature, the other is the equilibrium (32) which is shifted to the right at higher temperatures:

$$NO_2^+.H_2O + NO_3^- \leftrightarrow 2HNO_3 \leftrightarrow N_2O_5 + H_2O \quad (32)$$

On the basis of their experiments on electrolysis of 80-100% nitric acid Swinarski and Bialozynski [53] came to the conclusion that the nitronium ion exists mainly in hydrated form $NO_2^+.nH_2O$.

Isolation of salts in which nitric acid is a cation. Hantzsch's experiments on the preparation of nitracid and hydronitracid perchlorates have also been verified. Ingold and his co-workers [36,34,39] have indeed prepared salts of empirical formula corresponding to $(H_3NO_3)^{2+}(C1O_4)_2^-$. They also stated that the substance was a mixture of nitronium perchlorate $(NO_2)^+(ClO_4)^-$ and the well known perchloric acid hydrate $(H_3O)^+ (ClO_4)^-$. They separated the two components by fractional crystallization from nitromethane. But they did not succeed in the preparation of the compound $(H_2NO_3)^+(ClO_4)^-$.

To Weber's compound (p. 12) the formula of nitronium pyrosulphate is at present assigned $(NO_2)^+(HS_2O_7)^-$.

Examination of Raman and infra-red absorption spectra (which will be discussed later) confirmed the nitronium salt structure of all these compounds.

Ingold and his co-workers regarded nitric anhydride as nitronium nitrate $(NO_2)^+(NO_3)^-$ (see also eqn. 24). They obtained nitronium di- and trisulphates by treating nitric anhydride with SO_3:

$$(NO_2)_2^+ (S_2O_7)^{2-} \text{ and } (NO_2)_2^+ (S_3O_{10})_2^{2-}$$

Woolf and Emeléus [54] have prepared a number of other crystalline nitronium salts, for example:

$$NO_2^+ HS_2O_7^-$$
$$(NO_2^+)_2S_2O_7^{2-}$$
$$(NO_2^+)_2S_3O_{10}^{2-}$$
$$NO_2^+BF_4^-$$
$$NO_2^+SbF_6^- \text{ etc.}$$

Examination of the nitric acid spectrum (alone and in mixture with sulphuric acid)

Ultra-violet absorption spectrum. The first investigations into the ultra-violet absorption spectra of nitric acid, containing certain quantities of water, were carried out by Hartley [55]. He observed that the band at about 302 mμ characteristic for the nitrate ion disappears gradually with increase in concentration of nitric acid.

Among other investigations special attention should be paid to Schafer's in-

vestigations [24] between 1910 and 1916 referred to above, and also to the work of Halban and Eisenbrand [18].

Halban and Eisenbrand investigated the absorption spectrum of nitric acid at concentrations up to 68% (15.3 N) and noted the decrease in the intensity of the NO_3^- ion band with increasing concentration. They also observed a maximum at 265 mμ in the spectrum of solutions of anhydrous acid in anhydrous ether and attributed this to the presence of the unionized NO_2-OH molecule (Fig. 6). However, Hantzsch did not confirm this part of their work He found

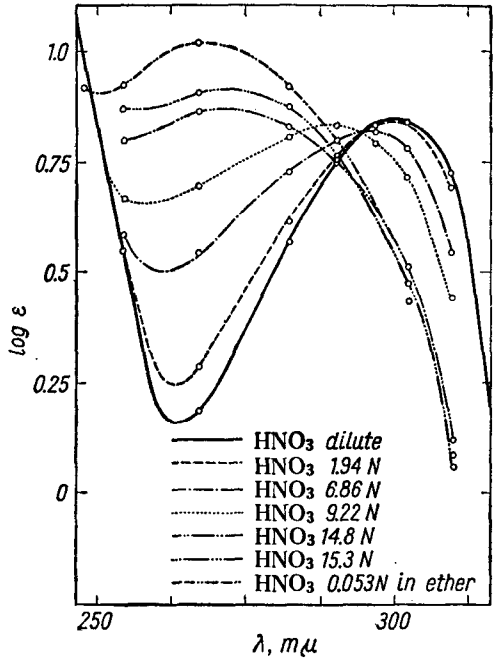


FIG. 6. Ultra-violet absorption spectra of nitric acid (Halban and Eisenbrand [18]).

no maximum in the absorption curve of 100% nitric acid, nor in the curve of a solution of nitric acid in anhydrous ether. He did note, however, that a band appeared on addition of a trace of water to such an ethereal solution.

Further experiments on ultra-violet absorption spectra of nitric acid in organic solvents have been carried out by a number of authors (Dalmon and Bellin [56], Kortiim [57]. Eventually R. N. Jones, Thorn et al. [58] expressed the view that nitrogen pentoxide is present in nitric acid of 95-96% and higher concentrations.

This was based on the following observations. At concentrations between 80 and 95%, an undissociated NO_2OH predominates which would be responsible for the absorption maximum near 260 mμ. This molecule or ion ("260 mμ chromogen") is present in maximal concentration at 91 to 92%. At 95 to 96%, changes occur in the spectrum which can be attributed to the presence of free

N_2O_5 in the solution. The failure of Hantzsch to find an absorption maximum in the solution of nitric acid in ether was, according to Jones and his co-workers, due to the presence of N_2O_5 in his acid. Indeed, these authors reported that solutions of N_2O_5 in nitric acid do not show a maximum (Fig. 7).

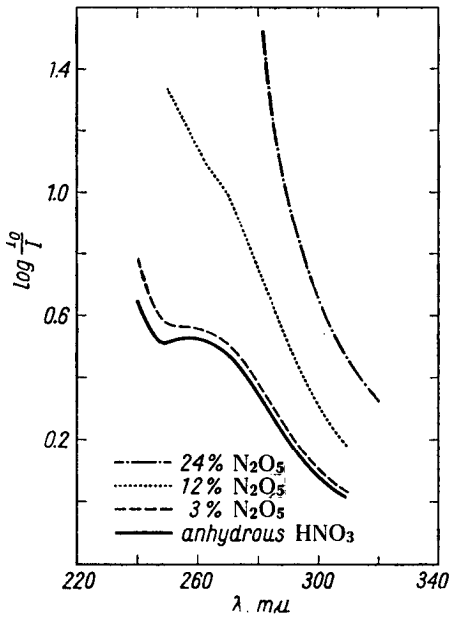
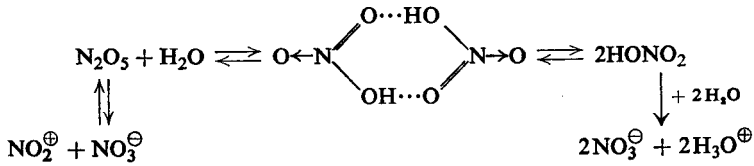


FIG. 7. Ultra-violet absorption spectra of solutions of N_2O_5 in anhydrous nitric acid. (R. N. Jones, Thorn, Lyne and E. G. Taylor [58]).

Jones expressed the view that the identification of "260 mμ chromogen" with undissociated nitric acid molecule (Hantzsch's pseudo-acid) is largely a speculative hypothesis for which there is insufficient evidence. He suggested that the 260 mμ band is produced by the NO_2^+ ion or by the undissociated N_2O_5 molecule. The high intensity of this absorption may obliterate the weak absorption of the nitrate ion at 302 mμ.

He summarized his views in the following system of equilibria:



(33)

Spasokukotskii [59] explained the results of these investigations in a similar way. He believed that the absorption maximum at 265 mμ corresponds to the nitronium ion NO_2^+, which is formed by a process of "self-ionization":

$$3HNO_3 \text{ <-> } NO_2^+ + H_3O^+ + 2NO_3^- \qquad (34)$$

which takes place together with the ordinary ionization:

$$HNO_3 + H_2O \leftrightarrow H_3O^+ + NO_3^- \quad (35)$$

Increase in concentration involves the formation of N_2O_5, consequently the concentration of NO_2^+ ions decreases the equilibrium of the reaction

$$NO_3^- + NO_2^+ \leftrightarrow N_2O_5 \quad (24)$$

being shifted to the right (compare the reaction on p. 19).

The maximum absorption band at 5% water corresponds to the shifting of the equilibrium to the left, when more NO_2^+ is formed.

In view of the practical application of solutions of ammonium nitrate in nitric acid in the Koffler-Bachman process for the manufacture of Cyclonite (Vol. III.)

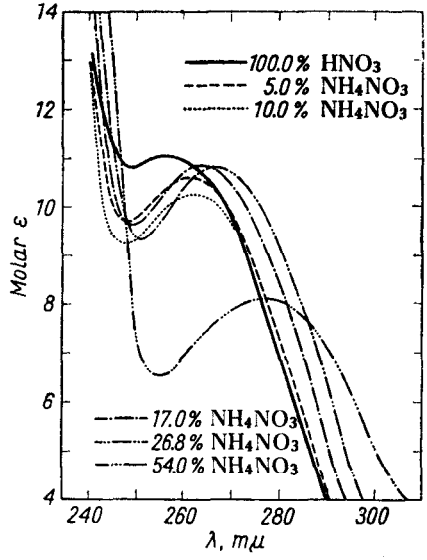


FIG. 8. Ultra-violet absorption spectra of nitric acid-ammonium nitrate solutions (R. N. Jones and Thorn [58a]).

the investigations of these solutions by R. N. Jones and Thorn [58a] are important. They examined solutions containing up to 54 g of ammonium nitrate in 100 g of solution. The results are recorded in Fig . 8. Small additions of ammonium nitrate cause a decrease in the intensity of the absorption maximum near 262.5 mμ. Further addition of ammonium nitrate then causes the intensity of absorption to increase, and it falls again at a higher concentration. The considerable bathochromic shift of the absorption maximum in a mixture containing 54% of NH_4NO_3 is probably caused partly by the additive effect of the nitrate ion absorption maximum at 301.5 mμ contributed by the ion NO_3^- of the added salt.

Raman spectrum. Extensive Raman spectrum studies have played a special role in the elucidation of the structure of nitric acid. They have thrown a good

deal of light on the changes which nitric acid undergoes on dilution with water, sulphuric acid, oleum, etc.

Chedin [6,60,61] gave the following results of the examination of the nitric acid Raman spectrum at concentration of the acid from 6.3 to 99.8% (Table 1).

TABLE 1

THE RAMAN LINES OF NITRIC ACID AT DIFFERENT CONCENTRATIONS

99.8%	95%	89.%	64%	52.1%	30.2%	24.5%	6.3%
611 cm-1	613 cm^{-1}	620 cm^{-1}	642 cm^{-1}	657 cm^{-1}	—	—	—
674	678	681	693	702	718 cm^{-1}	717 cm^{-1}	—
922	923	932	957	969	990	—	—
1048	1048	1052	1053	1053	1053	1053	1053 cm^{-1}
1103	—	—	1124	1128	—	—	—
1295	1300	1306	1308	1315	—	—	—
1537	1537	—	—	—	—	—	—
1679	1679	1679	1686	—	—	—	—

According to Chédin, the Raman line at 1050 cm^{-1} can be assigned to the NO_3^- ion.

Chédin and Fénéant [62] found the following bands and lines in their further investigations of high frequency Raman spectra:

weak lines at { ~2550 cm^{-1}, ~2700, ~3150

and a strong line at 3400

On adding water the intensity of the band 3400 cm^{-1} decreases while that of the other bands increases. It seems very likely that the bands at ~3400 cm^{-1} belong to nitric acid molecules linked by hydrogen bond (pp. 7-8), while the lines at 2550, 2700 and 3150 cm^{-1} probably belong to nitric acid hydrate molecules.

Médard [48] and in 1935 Chédin [60] stated, that solutions of nitric acid in sulphuric acid produced a Raman spectrum with two characteristic lines: at 1050 and 1400 cm^{-1}. As we have seen the 1050 cm^{-1} line is present in nitric acid of various concentrations, while the line 1400 cm^{-1} has not been observed.

Further investigations of Chédin [60a-62] and of Susz, Briner and Favarger [63] have shown that a solution of nitric anhydride (N_2O_5) in nitric acid produces both 1050 and 1400 cm^{-1} lines. From this the assumption has been advanced that the two lines indicate the presence of N_2O_5 in mixtures of nitric and sulphuric acids. Thus it seemed that Sapozhnikov's theory (p, 10) had been confirmed. However, further investigations have shown that this interpretation of the results is not quite right. For Chédin stated that solutions of N_2O_5 in carbon tetrachloride, chloroform, nitromethane and phosphorus oxychloride produced the 707, 860, 1033, 1240 and 1335 cm^{-1} lines (in addition to the solvent line), while there were

no 1050 and 1400 cm^{-1} lines, whereas solid N_2O_5 showed the presence of both the 1050 and 1400 cm^{-1} lines.

On the grounds of Walden's observations (in his cryometric studies), that nitric anhydride exists in $POCl_3$ solution in a non-associated form, and that according to Russ and Pokorny [64] it is associated when in solid form, Chédin has come to a conclusion that the Raman 1050 and 1400 cm^{-1} lines correspond to associated N_2O_5, while the 707, 860, 1033, 1240, and 1335 cm^{-1} lines correspond to the non-associated, monomolecular form of N_2O_5. Consequently N_2O_5 in nitric acid or in nitric and sulphuric acids solution would appear to exist in an associated form.

As the presence of the nitronium ion NO_2^+ in nitric acid and in its mixtures with sulphuric acid had again been suggested, the view has been expressed that the 1400 cm^{-1} line should be assigned to that ion, and the 1050 cm^{-1} line to the nitrate ion NO_3^- (Chedin drew attention at an earlier date to that). It was also revealed that the hydrosulphate ion (HSO_4^-) present in sulphuric acid and in mixtures of sulphuric and nitric acids also produces the 1050 cm^{-1} line.

Nitric anhydride produces a spectrum composed of the two lines, since it undergoes dissociation according to the eqn. (24) given on p. 15.

According to the eqn. (18) on p. 15, nitric acid also yields the nitronium ion with sulphuric acid.

This interpretation of the Raman spectrum was verified in 1946 by Ingold and his co-workers [36] for mixtures of nitric acid with other concentrated acids. Thus, for example, mixtures of nitric and perchloric or selenic acids produce a high intensity 1400 cm^{-1} line, but not a trace of the 1050 cm^{-1} line. Instead of the latter, lines corresponding to the perchlorate and selenate ions appear.

On the basis of these experiments it has been established that the 1400 and 1500 cm^{-1} lines correspond to completely different molecules. It has also been established decisively that the 1400 cm^{-1} line appears on the addition of another strong acid to nitric acid and that most likely it corresponds to the NO_2^+ ion, which is formed in such a solution.

In 1936 Chédin [60a] also examined the Raman spectrum of the solution of nitric acid in oleum. He observed, of course, the 1400 cm^{-1} line, and also another one, between 1075 and 1095 cm^{-1}. At first the two lines had been assigned to the $N_2O_5(SO_3)_n$ complex. Yet the work of Millen and Ingold [36,37] has shown that $KHSO_4$ also produces a line ranging from 1075 to 1095 cm^{-1}; the frequency varied with concentration. At present the line is assigned to the hydropyrosulphate ion $HS_2O_7^-$ which is probably formed according to the equation:

$$HSO_4^- + H_2S_2O_7 \leftrightarrow H_2SO_4 + HS_2O_7^- \qquad (36)$$

Since in this system the HSO_4^- ion is also present, giving the 1050 cm^{-1} line, the two frequencies 1095 and 1050 cm^{-1} are superimposed and the resultant frequency is 1095-1075 cm^{-1}, depending on the intensity of the 1050 cm^{-1} frequency.

The Raman spectra of solutions $N_2O_5 + nH_2O$, with $n>1$, confirm the view that nitric anhydride dissociates according to the equation presented on p. 19.

The anhydrous nitric acid which is formed in this system is dissociated into the same ions (eqn. (1) p. 6).

The diagram (Fig. 9) shows the concentration of NO_2^+ ions in various nitrating mixtures determined by measurements of the intensity of Raman lines. The limits

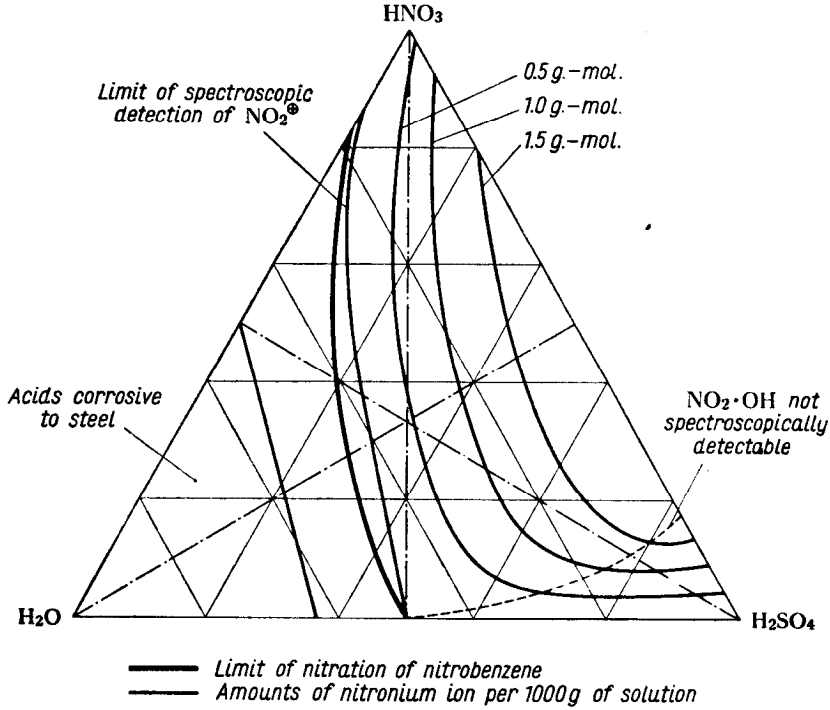


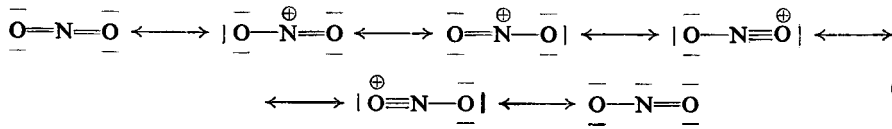
FIG. 9. Concentration NO_2^+ ions in mixtures HNO_3-H_2SO_4-H_2O (Gillespie and Millen [11]).

of the ability to nitrate nitrobenzene by various mixtures almost coincide with the limit of detectability of NO_2^+ by the Raman spectrum analysis.

According to Chédin and Fénéant [62a] the maximum concentration of NO_2^+ (ca. 4.5 g-ion/l.) exists in the solution of 20-40% HNO_3 in sulphuric acid.

Structure of the nitronium (nitryl) ion NO_2^+

In 1941 Titov [35] considered the structure of the nitronium ion as a number of resonating structures :



(37)

Titov postulated that the NO_2^+ ion may be regarded as isosteric with carbon dioxide O=C=O, thus suggesting a linear structure for the ion.

Indeed, according to Bennett, Brand and Williams [43] the fully symmetrical structure of NO_2^+

$$O{=}\overset{\oplus}{N}{=}O$$

should be accepted on the basis of the Raman spectrum. They also pointed out the similarity between CO_2 and NO_2^+, the only difference being that NO_2^+ ion has one extra unit charge on the central nucleus as compared with the CO_2 molecule. Therefore it is to be expected that the frequency of fundamental vibration of NO_2^+ should be somewhat higher than for that of CO_2 (ca. 1320 cm^{-1}). These considerations are consistent with the observed value 1400 cm^{-1} for NO_2^+. Moreover the degree of depolarization (ca. 0.20 according to Chédin) confirms that the line must arise from a totally symmetrical vibration.

This structure was confirmed in 1948 by Cox, Jeffrey and Truter [65] by X-ray examination of nitronium perchlorate. The distance N-O was found to be 1.1 Å (Fig. 10). Grison, Eriks and Vries [65a] gave the figure 1.154±0.01 Å.

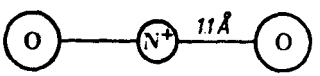


FIG. 10. Structure and bond distances in NO_2^+ cation.

Infra-red absorption spectra. For a long time the experimental difficulty of working with nitric acid in the infra-red region due to corrosion of the cells by nitric acid hindered examination of the infra-red absorption spectrum of nitric acid. Originally therefore, only the near infra-red region was studied.

Thus Badger and Bauer [7] examined the spectrum of 100% nitric acid vapour alone and in dioxane solution in the region near 1 μ. Dalmon [8,49], Dalmon and Freymann [9], and Freymann [66] have studied the spectra of nitric acid and its solutions in dioxane, carbon tetrachloride and water.

By using glass and polyethylene cells with silver chloride windows Ingold and his co-workers [40] succeeded in examining the infra-red spectra of nitric and deuteronitric acid vapour, Fréjacques [67] examined the spectra of liquid and gaseous nitric acid, and Bethel1 and Sheppard [68] investigated the infra-red spectra of fuming nitric acid.

Fréjacques failed to detect the NO_2^+ bands in the spectra and this cast some doubt on the existence of the NO_2^+ ion in concentrated nitric acid. However, Marcus and Fresco [69] in their extensive investigation of the infra-red spectra of nitric acid discovered that the absorptivity of the NO_2^+ ion is very low. The NO_2^+ bands can be observed only when a thick layer (18.4 μ) of nitric acid is used. The NO_2^+ frequencies are: 2360 and 3745 cm^{-1}. (The Raman frequency 1400 cm^{-1} cannot be present in the infra-red spectrum as it is produced by fully symmetrical vibrations of NO_2^+).

The intensity of the band 2360 cm^{-1} is enhanced by the addition of nitronium fluoroborates, sulphuric acid, phosphorous pentoxide, or small amounts of acetic

anhydride. It is produced by addition of sodium nitrate, potassium dihydrogen phosphate, water or larger amounts of acetic anhydride.

Recently Hofman, Stefaniak and T. Urbanski [70] examined the spectra of nitric acid alone and in solutions in sulphuric acid. The following are the frequencies they obtained for nitric acid of 98.2-99.5% concentration:

1665 cm^{-1} a medium band, assymmetric stretching vibrations of the NO_2 group
1368 cm^{-1} a very strong band of the nitrate ion (NO_3^-)
1297 cm^{-1} a strong band, symmetric stretching vibrations of the NO_2 group
948 cm^{-1} a weak band, bending vibrations of NO_2 group
774 cm^{-1} a weak band, deformation by out-of-plane vibrations.

Dilute nitric acid (6%) gives bands at 3400 and 1642 cm^{-1} which should be assigned to the stretching and deformation vibrations, respectively of the OH group in water. Two more bands at 1385 and 770 cm^{-1} have the same origin as in concentrated acid.

Vapour pressure measurements

The exceptionally low vapour pressure of HNO_3 in admixture with sulphuric acid is a proof that nitric acid is present, in such a mixture, not in the free state, but as a compound. Gelfman [69] measured the vapour pressures of mixtures of $HNO_3 + H_2SO_4 + SO_3$ and drew some conclusions from the values obtained. He stated that the vapour pressure minimum corresponds to the weight ratio SO_3: HNO_3 =2.5. The vapour pressure rises as this ratio increases-at first slowly, then more rapidly, especially when the ratio SO_3: HNO_3 = 6.5. Near the minimum, the vapour consists chiefly of HNO_3 and near the maximum mainly of SO_3. Gelfman suggested on the basis of Sapozhnikov's work (p. 10) and that of Chédin on the Raman spectra of nitric and sulphuric acid mixtures, that the vapour pressure minimum is due to the formation of a stable compound $N_2O_5.4SO_3$, and the less stable compounds $N_2O_5.3SO_3$ and $N_2O_5.5½SO_3$.

This view has been criticized by Spasokukotskii [59] who explains Gelfman's observations in the light of Brand's equilibrium equations.

Spasokukotskii points out that undissociated compounds of the $N_2O_5.nSO_3$ type cannot exist in solution in sulphuric acid since both nitric acid and nitric anhydride undergo dissociation, yielding the NO_2^+ ion. At the weight ratio SO_3:HNO_3 = 2.5, the molar ratio is 2 which would be consistent with the equation:

$$HNO_3 + 2SO_3 \leftrightarrow NO_2^+ + HS_2O_7^- \quad (38)$$

Besides, it would just correspond to Gelfman's compound $N_2O_5.4SO_3$. In the case of smaller amounts of SO_3 the equation would be:

$$2HNO_3 + 3SO_3 \leftrightarrow 2NO_2^+ + S_2O_7^{2-} + H_2SO_4 \quad (39)$$

which again would correspond to another compound suggested by Gelfman, viz. $N_2O_5.3SO_3$.

Vandoni [72] repeated the experiments of Sapozhnikov on the vapour pressure of HNO_3 over mixtures of HNO_3-H_2SO_4-H_2O using an improved technique. In the main, he confirmed the earlier results, but he introduced some corrections to the figures obtained by Sapozhnikov. Thus he used nitric acid free from nitrogen oxides which were present in the acid used by Sapozhnikov. Vandoni has shown

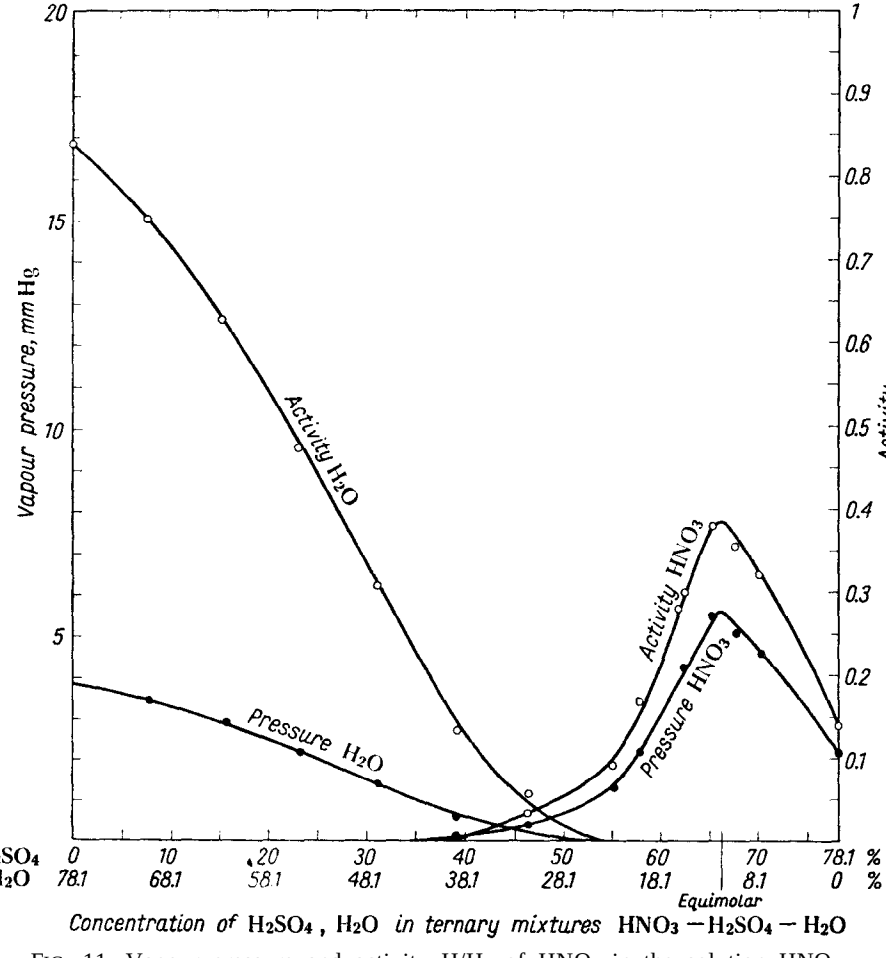

Vapour pressure, mm Hg
Activity
Activity H2O
Activity HNO3
Pressure H2O
Pressure HNO3
H2SO4
H2O
0 10 20 30 40 50 60 70 78.1 %
78.1 68.1 58.1 48.1 38.1 28.1 18.1 8.1 0 %
Equimolar
Concentration of H2SO4, H2O in ternary mixtures HNO3 — H2SO4 — H2O

FIG. 11. Vapour pressure and activity H/H_0 of HNO_3 in the solution HNO_3-H_2SO_4-H_2O containing 21.9% HNO_3 (Vandoni [72]).

that the absorption of vapours of nitric acid by potassium (the method applied by Sapozhnikov) is not complete. Instead of HNO_3 vapour pressure values, Vandoni utilized the activity of HNO_3, i.e. the ratio H/H, between the vapour pressure of HNO_3 over the surface of the solution (H) and the vapour pressure of pure HNO_3 (H_0 = 14.1 mm Hg at 0°C).

Vandoni's diagrams of the activity of HNO_3 and H_3O, when the content of HNO_3 is 21.9 and 50% (i.e. in the most common nitrating mixtures) are given in Figs. 11 and 12 respectively.

The triangular diagram of Sapozhnikov was modified by Vandoni, on the basis of his own experimental data, to the diagram of HNO_3 activities (Fig. 13). Thus instead of isobars of HNO_3 vapour pressures he constructed curves of equal activities. The advantage of such a diagram is, among other things, that unlike vapour pressure, activity is independent of temperature.

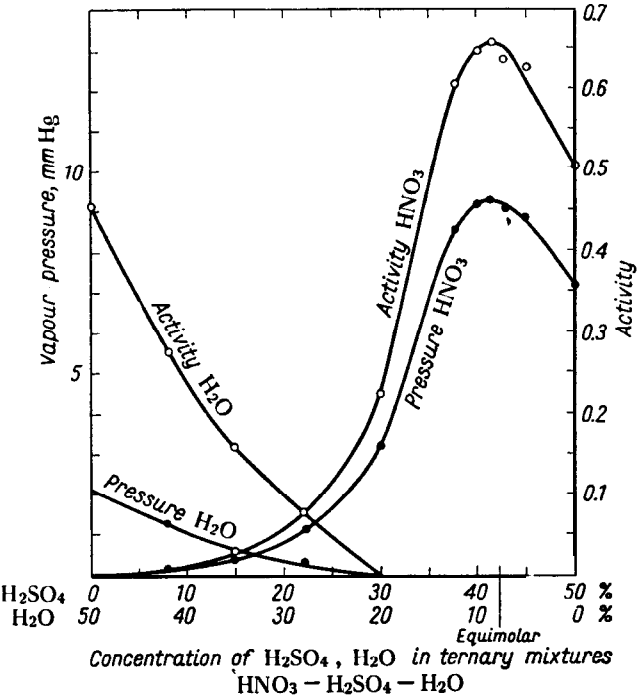


FIG. 12. Vapour pressure and activity H/H_0 of HNO_3 in the solution HNO_3-H_2SO_4-H_2O containing 50% HNO_3 (Vandoni [72]).

Activity as a function was introduced by Lewis in 1908, and a full description was given by Lewis and Randall [74] in 1923. The activity a_i of a substance "i" can be defined [75.76] as a value corresponding to the mole fraction of the substance "i" in the given phase. This value is in agreement with the thermodynamic potential of the ideal mixture and gives the real value of this potential.

Lewis and Randall give an example of calculating the activity of a solute from its vapour pressure. When a solution is in equilibrium with the vapour of the solute x_2, we may measure the vapour pressure of x_2 over a range of concentrations, and by knowing the fugacity of the vapour at each pressure we may obtain the activity of the solute in the solution. When we may assume that the vapour is a perfect gas, the activity a_2 in the solution may be taken as proportional to p_2, the vapour pressure of the solute. Hence. as we pass from the mole fraction N_2 to an infinitely dilute solution of mole fraction N^x_2

$$\frac{a_2}{p_2} = \frac{a_2^x}{p_2^x}$$

Now by Henry's law, 2 approaches a constant value, at infinite dilution which may be

denoted by $\frac{N_2^x}{p_2^x}$ But by definition of our standard state, $a_2^x = N_2^x$, and therefore at any concentration

$$a_2 = p_2 \frac{N_2^x}{p_2^x}$$

$$\frac{a_2}{N_2} = \frac{p_2}{N_2} \cdot \frac{p_2^x}{N_2^x}$$

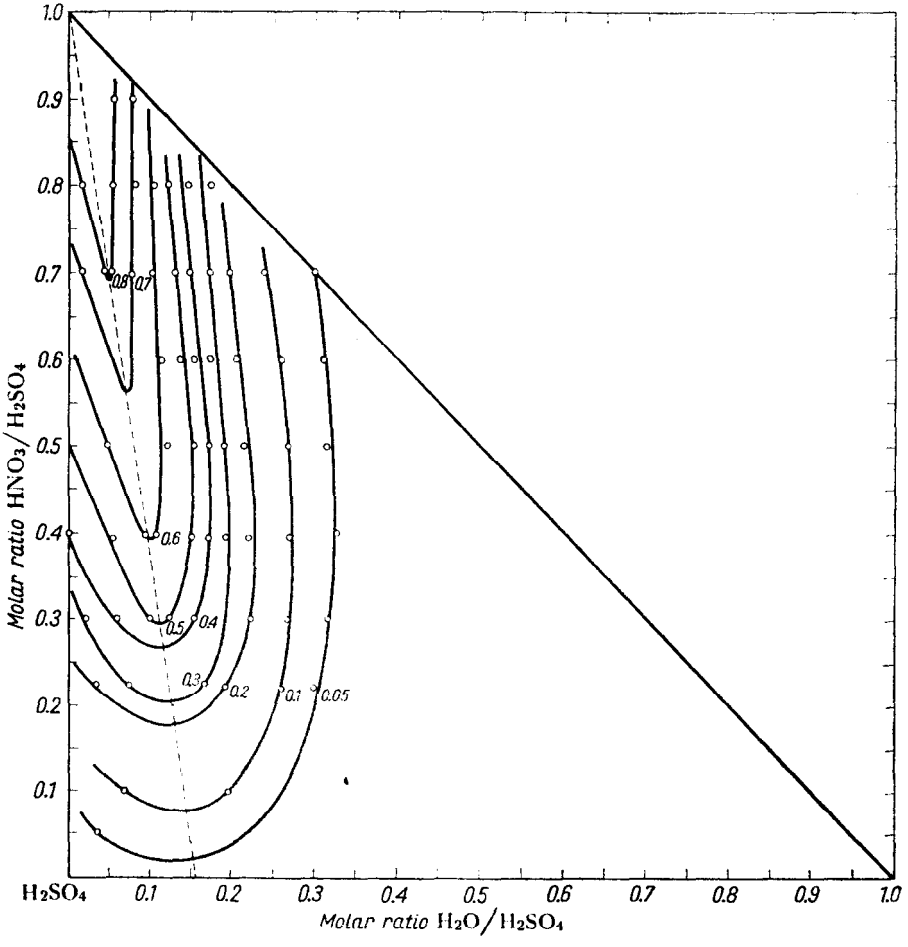


FIG. 13. Activity H/H_o of HNO_3, in solutions HNO_3-H_2SO_4-H_2O at 0°C (Vandoni [72]).

Thermochemical measurements

On the basis of measurements of the heat generated on mixing nitric and sulphuric acid Gelfman [71] drew the conclusion that the two acids do not yield any stable molecular compounds.

On the basis of similar measurements of the heat of solution of SO_3 in nitric

acid it was found that the compounds of HNO_3 and SO_3 are more stable. According to Gelfman the compound $HNO_3.2SO_3$ can be obtained in a crystalline form, Moreover, Gelfman believed that the compounds $HNO_3.18SO_3$ and $3HNO_3.SO_3$ do in fact exist.

Density measurements

Klimova, Zaslavskii and their co-workers [77,77a] have measured the densities of anhydrous nitric and sulphuric acid mixtures. They obtained characteristic slopes in the density curve of the mixtures at molar ratios HNO_3:H_2SO_4 = 1:2 and 1: 1. Hence they inferred that in the solution containing 24 by wt.% of HNO_3, the cation $H_3NO_3^{2+}$ is present; with a decrease in H_2SO_4 concentration this is converted into the $H_2NO_3^+$ cation (39 by wt.% HNO_3).

Moreover, interpretation of the density curves of the acids and water mixtures led them to the conclusion that on gradually adding water, hydrolysis of Hantzsch's ions occurs:

$$H_3NO_3^{2+} + H_2O \text{ <-> } H_2NO_3^+ + H_3O^+ \quad (40)$$

$$H_2NO_3^+ + H_2O \text{ <-> } HNO_3 + H_3O^+ \quad (41)$$

Since according to Hantzsch the $H_2NO_3^+$ ion is the principal nitrating agent, these reactions could account for the fact that organic compounds are best nitrated with a nitric and sulphuric acid mixture with a water content of 10%.

Viscosity measurements

Measurements of the viscosities of nitric acid-sulphuric acid-water mixtures have been the subject of research work by several authors. Zaslavskii, Klimova and Guskova [78] have observed a maximum, corresponding to the combination of ions:

$$(H_3NO_3)^{2+} \quad (HSO_4)_2^-$$

With increase in water content the maximum in the curve shifts towards lower concentrations of HNO_3 and disappears when the dilution has attained a degree corresponding to 1 mole of water for 1 mole of the above compound.

Recently Swinarski and Dembinski [51] and Swinarski and Piotrowski [52], have examined the viscosities of the three component solutions HNO_3-H_2SO_4-H_2O. The diagram in Fig. 14 shows the results of these investigations, in terms of changes in viscosity with increase in HNO_3 content. The authors pointed out a similarity between the viscosity curve they obtained and the electric conductivity curve (see Fig. 4, p. 18).

The curve shows a distinct maximum at 20 mole % HNO_3. The authors explained this by postulating the formation of a hydrated NO_2^+ ion:

$$HNO_3 + 2H_2SO_4 + H_3NO_3^{2+} + 2HSO_4^- \quad (31)$$

An increase in concentration of HNO_3 causes a decrease in viscosity, presumably because of dissociation:

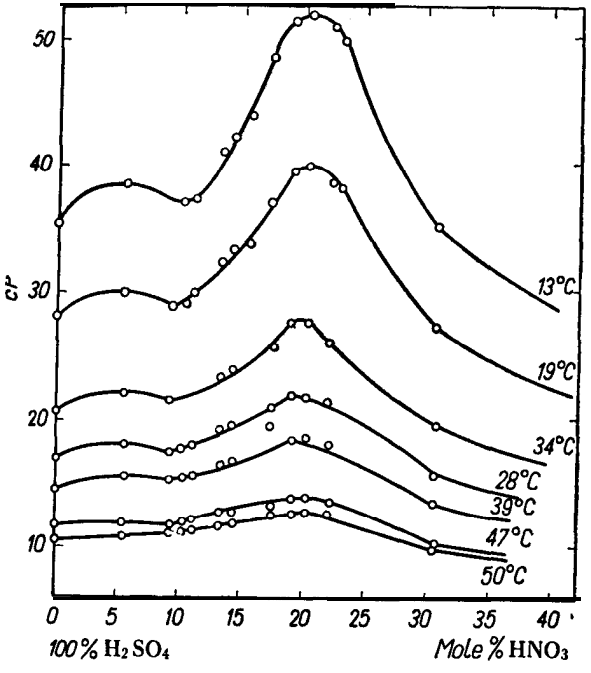


FIG. 14. Viscosity of solutions HNO_3-H_2SO_4-H_2O. Change in viscosity with increase of HNO_3 content at various temperatures (Swinarski and Piotrowski [52]).

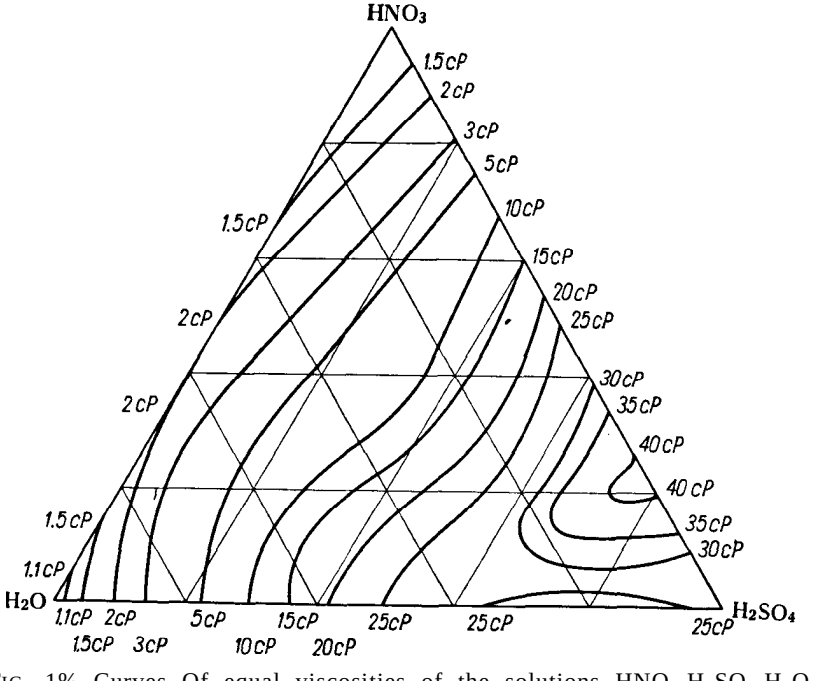


FIG. 1% Curves Of equal viscosities of the solutions HNO_3-H_2SO_4-H_2O (Hackel, T. Urbanski, Kutkiewicz and Sternidski [80]). (Composition in mole %)

$$H_3NO_3^{2+} \rightarrow NO_2^+ + H_3O^+ \quad (16)$$

Krejci, Novotny and Ruzicka [79] have also recently examined the viscosities of mixtures of nitric and sulphuric acids with water from the point of view of their practical importance.

In 1961 Hackel, T. Urbanski, Kutkiewicz and Sterninski [80] have examined the viscosities of these mixtures and presented the results as the curves of a triangular diagram (Fig. 15). It can be seen that a maximum viscosity exists for the solution containing 20-25 mole % of sulphuric acid, i.e. for the compound $(HNO_3)_3.H_2SO_4$.

APPLICATION OF KINETIC STUDIES TO ELUCIDATE THE STRUCTURE OF NITRATING MIXTURES

The first attempts to study nitration kinetics were made by L. Meyer and coworkers [81,82]. It was in their publication that for the first time a statement appeared that the nitration reaction is irreversible and that its rate decreases with time.

Martinsen [83] observed already in 1905 that the rate of nitration of nitrobenzene with a mixture of nitric and sulphuric acids depends on the concentration of sulphuric acid, viz. it increases with the concentration up to 88.7% H_2SO_4, after which further increase in sulphuric acid concentration results in a decreasing rate of nitration.

In 1924, Klemenc and Schöller [34] stated that *m*- xylene-2,6-disulphonic acid is nitrated with nitric anhydride in sulphuric acid twice as rapidly as when it is nitrated with nitric acid in sulphuric acid, the molar concentration being the same. This was illustrated in the following scheme, where the nitrating agent was denoted by X:

$$\begin{array}{c} \tfrac{1}{2}N_2O_5 \\ \uparrow\downarrow \\ RH + X = RNO_2 + H_2O \\ \uparrow\downarrow \\ HNO_3 \end{array} \quad (42)$$

It is clear, that the scheme corresponds to the eqn. (5). It follows that the concentration of NO_2^+ ions from N_2O_5 is twice as high as that of NO_2^+ ions from HNO_3 (see eqn. 19).

J. A. Hetherington and Masson [84], basing their views on the studies of benzene nitration kinetics, stated that the reaction of nitrobenzene nitrated with a mixture of HNO_3, H_2SO_4 and H_2O would stop before all the nitric acid was used if the amount of sulphuric acid in the mixture was insufficient to form the $H_2SO_4.H_2O$

hydrate with water, originally present in the mixture and formed in the reaction. Hence they proposed the following equilibrium equation for the nitrating mixture:

$$H_2SO_4, + H_3O+ + NO_3^- \text{ <-> } H_3O^+ + HSO_4^- + HNO_3 \quad \textbf{(43)}$$

The more the equilibrium is shifted to the right the higher the reaction rate.

According to Hetherington and Masson undissociated nitric acid is a nitrating agent and in its interaction with nitrobenzene a complex with the $C_6H_5NO_2H^+$ cation is formed, which subsequently reacts with HNO_3 to yield dinitrobenzene.

In his experiments on the nitration of naphthalenesulphonic acid Lantz [85] found that the rate of nitration with a nitric acid and sulphuric acid mixture was highest when the concentration of sulphuric acid used was about 90% H_2SO_4

From these experiments, and on the basis of the Brönsted acids and bases theory, as well as Hantzsch's theory, Lantz has concluded that in a nitrating mixture the hydrated sulphuric acid $H_2SO_4.H_2O$ acts as a base towards anhydrous sulphuric acid. Thus an equilibrium acid-base system is established:

$$H_2SO_4 + nH_2SO_4*H_2O \text{ <-> } HSO_4^- + H_2SO_4.H_3O^+ \quad (44)$$

The HSO_4^- ions formed participate in the reaction

$$2H_2SO_4 + HNO_3 \text{ <-> } 2HSO4- + H_3NO_3 \quad (31)$$

shifting the equilibrium of reaction (31) to the left, which results in a decrease in concentration of $H_3NO_3^{2+}$ cations and in an increase in concentration of HNO_3.

These substances-the cation and the undissociated acid-both have nitrating properties.

In the case of higher concentrations of water, the following reaction might take place :

$$HNO_3 + H_2O \text{ <-> } NO_3^- + H_3O^+ \quad (35)$$

Then the nitrating action of nitric acid would stop.

Lantz also draws attention to the fact that the equilibrium of reactions (44) and (31) are greatly affected by the nature of the substance, being nitrated. The rate of the nitration reaction also depends on the structure of the nitrated substance. The more basic groups it contains the more distinct the acidic character of the nitrating agent and the more vigorous the nitration reaction.

Westheimer and Kharasch [86] also chose reaction kinetics as a method of studying the actual composition of nitrating mixtures. They found, that the rate of a nitration reaction depends chiefly on the acidity of the medium and not on its dehydrating properties. Therefore, the reaction rate is highest when 90% sulphuric acid is used as a solvent for nitric acid, while the reaction remains unaffected when a substance of strong dehydrating properties such as phosphoric anhydride is added to the mixture.

When 90% sulphuric acid is used as a solvent, increase in concentration of HNO_3 in a nitrating mixture results in reducing the rate of nitration, since the acidity of the mixture is reduced. In the case of more concentrated sulphuric acid

temperatures, according to the data given by several authors. The shapes of the curves are the same for all measurements.

Bennett's explanation of the existence of a maximum in the nitration rate at the sulphuric acid concentration mentioned above is as follows. Since in nitration

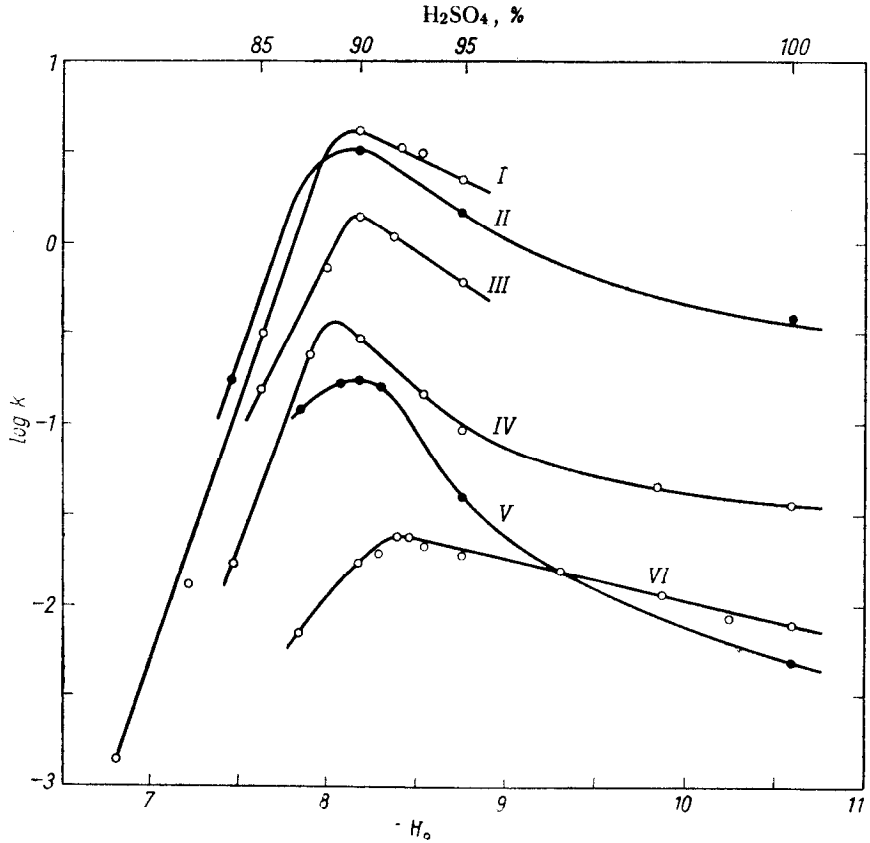


FIG. 16. Variation of the rate of the nitration constant against the concentrations of sulphuric acid in the nitrating mixture: I - Nitration of nitrobenzene at 25°C (Westheimer and Kharasch [89]). II - Nitration of nitrobenzene at 25°C (Martinsen [83]); III - Nitration of dinitromesitylene at 25°C (Westheimer and Kharasch [86]); IV - Nitration of nitrobenzene at 0°C (Martinsen [83]); V - Nitration of anthraquinone at 25°C (Latter and Oda [32]); VI - Nitration of dinitrotoluene at 90°C (Bennett [S]). He is Hammett acidity function defined by the equation

$$H_0 = -\log\left(\frac{a_H f_B}{f_{BH^+}}\right).$$

Reproduced from Gillespie and Millen [11].

with the nitronium ion a proton is split off from the nitrated substance (reaction 22, p. 60) the presence of proton acceptors in the nitrating mixture should favour the nitration reaction. Such a role is played for example by HSO_4^- ions, sulphuric acid, which is able to form the $H_3SO_4^+$ cation with the proton, and HSO_7^- ions, that exist in mixtures containing oleum.

Thus, the nitration rate would depend on two factors: on attaching the nitronium

ion and on removing, i. e. binding, the proton. An increase in water concentration in a nitrating mixture gives rise to an increase in the HSO_4^- ion concentration and thus enhances the process of removing the proton from the nitrated compound. Yet, at the same time, it reduces the nitronium ion concentration. Changes in the nitration rate with the water content of a nitrating mixture would be the resultant of the sum total of the two effects.

However, investigations on the nitration of deuterobenzene raised doubts about the influence of the velocity of splitting off the proton on the nitration reaction rate.

By using deuteronitric acid Ingold, Raisin and Wilson [38] established that no substitution of hydrogen atoms by deuterium atoms occurred (in this respect the action of deuteronitric acid differs from that of deuterosulphuric acid, leading to the formation of deuterated benzenes up to the fully substituted hexadeuterobenzene).

From these results and later experiments (Ingold and co-workers [36,37, 39]) on the influence of solvents on the nitration rate Ingold came to the conclusion that splitting off the proton in the nitration of aromatics does not effect the reaction kinetics. This conclusion differed from that of Bennett and his co-workers [87].

Recently Melander [88] attempted to clarify the influence of the proton loss on the nitration reaction rate by investigating this process using a number of aromatic compounds: benzene, toluene, bromobenzene and naphthalene, in which one hydrogen atom had been replaced by tritium.

It is well known that there is no general rule applicable to the difference in the rates of the reactions involving compounds having hydrogen or its heavier isotopes ^2H (deuterium) and ^3H (tritium) in their molecules. In some cases the heavier isotopes react more slowly, in others more quickly.

Melander points out that unless hydrogen is firmly attached by a covalent bond and can change its position (as in tautomerism), heavy isotopes react more slowly. The influence of heavy water on the rate of neutralization of a pseudo-acid such as nitroethane, as observed by Wynne-Jones [89], may be cited as an example. According to him the rate of the reaction involving deuterium loss was about ten times lower than when the proton was lost.

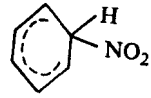
Melander in his experiments on sulphonation of the monotritero aromatics, triterobenzene and 4-triterobromobenzene, found the replacement of tritium by the sulpho group proceeded much more slowly than the replacement of protium (Hydrogen H).

However, on nitrating the following aromatic compounds, having one atom of hydrogen H replaced by tritium: triterobenzene, 2-triterotoluene, 4-triterotoluene, 2-triterobromobenzene and α– triteronaphthalene, Melander found that the rate of nitration of these compounds did not differ from the rate of nitration of hydrocarbons which did not contain heavier hydrogen isotopes.

Melander nitrated naphthalene to α– dinitronaphthalene and other compounds to dinitro derivatives. When nitrating ordinary aromatic compounds (not containing heavier hydrogen isotopes) with a nitrating mixture containing water plus a

quantity of tritium oxide, he also investigated whether the hydrogen-tritium exchange was taking place and found that in these conditions the exchange either did not occur at all or was very insignificant. These observations confirmed those of Ingold on benzene nitration with deuteronitric acid.

According to Melander, the experimental facts show that the nitration reaction is a two-stage mechanism. In the first stage the intermediate compound



would be formed and it is only in the second stage that the proton was split off.

Similar tests on nitration of monodeuterobenzene were carried out by W. M. Lauer and Noland [90]. They found that the deuterium content in the nitration products (nitro- and dinitrobenzene) was proportional to its content in the initial compound, thus confirming Melander's observations on tritium.

Bonner, Bowyer and G. Williams [91] stated that the rate of nitration of nitrobenzene with nitric acid in 97.4 and 86.7% sulphuric acid was much the same as the rate of nitration of pentadeuteronitrobenzene with the same mixture. Thus, the results obtained by W. M. Lauer and Noland and by Banner and his co-workers supported Melander's earlier observation, that the rupture of the C-H bond was not a determining factor for the rate of nitration of aromatic compounds.

All these investigations confirm that the nitration process is a two-stage substitution reaction, where the first slope consists in attaching the nitronium ion, according to eqns. (22) and (23), p. 60, or according to Melander (as above).

Bunton, Halevi and Llewellyn [92] studied the oxygen atom exchange between nitric acid and water, using heavy oxygen ^{18}O as the labelled element. They found that the higher the exchange rate, the higher the concentration of nitric acid. At low HNO_3 concentrations the reaction proceeded in the presence of nitrous acid. At high HNO_3 concentrations the presence of nitrous acid was not indispensable for the exchange.

When comparing the rate of this reaction with the rate of nitration of aromatic compounds with nitric acid of various concentrations, Bunton and Halevi [93] came to the conclusion that the oxygen exchange between nitric acid and water proceeded faster than the nitration reaction. It was only for high concentrations of HNO_3 and for readily nitrated compounds that the values of the rates of both the reactions were of the same order.

Bunton and Halevi have examined the following reactions (O* denotes heavy oxygen) :

$$HNO_3 + HNO_3 \leftrightarrow H_2NO_3^+ + NO_3^- \quad (a)$$

$$H_2NO_3^+ \leftrightarrow NO_2^+ + H_2O \quad (b)$$

nitration : $$NO_2^+ + RH \leftrightarrow RNO_2 + H^+ \quad (c)$$

oxygen exchange: $$NO_2^+ + H_2O^* \leftrightarrow H_2NO_3{}^{*+} \quad (d)$$

$$H_2NO_3{}^{*+} \leftrightarrow H^+ + HNO_3^* \quad (e)$$

and have inferred that both nitration and oxygen exchange involve formation (b) and destruction (c, d) of the nitronium ion. Reactions (c) and (d) are competitive with preference for reaction (d). The nitracidium ion is formed in reaction (d).

In 1948, Titov [35] also studied the problem of the existence of a maximum in the nitration rate at certain concentration of sulphuric acid. He assumed, like Hetherington and Masson, (see p. 33), that cations might be formed in nitration by the attachment of protons to nitro compounds, for example:

$$C_6H_5NO_2 + H^+ \rightarrow C_6H_5NO_2H^+$$

The $C_6H_5NO_2H^+$ cation undergoes a substitution reaction with much more difficulty than the nitro compound $C_6H_5NO_2$ itself, since the addition of a proton gives rise to a sharp drop of prototropic behaviour of the compound.

The rate of nitration of nitrobenzene to dinitrobenzene may be expressed, according to Titov, by the equation:

$$\frac{d[C_6H_4(NO_2)_2]}{dt} = k_m [NO_2^+] [C_6H_5NO_2^+] k_k [NO_2^+] [C_6H_5NO_2H^+]$$

It is only the first factor in the right side of the equation which affects the nitration rate, since the second factor is very small because of the low rate of nitration of the $C_6H_5NO_2H^+$ ion.

An increase in sulphuric acid concentration results in increase in the concentration of the $C_6H_5NO_2H^+$ cation, hence in a decrease in the $C_6H_5NO_2$ concentration which in turn brings about a decrease in the nitration rate. On the other hand the concentration of the NO_2^+ ion increases with increase in sulphuric acid concentration.

Titov believes, as in Bennett's interpretation, that summing up the two effects results in a maximum in the reaction rate at a certain concentration of H_2SO_4.

Ingold, Hughes and Reed [39] studied the kinetics of nitration of aromatic compounds with nitric acid only and found that it was a first order reaction. Its rate, V_N, may be expressed by an approximate equation:

$$V_N = k_1[ArH]$$

at $[HNO_3]$ = const.

Ingold and his co-workers [36,37,39] inferred from the results of their studies that the nitration rate, V_S, in the presence of sulphuric acid might be expressed roughly by the equation:

$$V_S = k_1[ArH][HNO_3]$$

In the nitration of numerous compounds, and particularly those containing many nitro groups, e.g. nitration of dinitro- to trinitro compounds, or nitro derivatives of naphthalene, which are sparingly soluble in a nitrating mixture, nitration takes place in a two-phase system: acid-organic compound, the acid phase being a saturated solution of the organic compound. If the compound is liquid at nitration temperature, then the organic liquid phase is a saturated solution of acid in the nitrated substance. In this case the reaction rate depends among other

things on the concentration of the organic compound in the acid, on the concentration of the acid in the organic compound, on the interfacial area and on the diffusion rate at the phase boundary. If a nitrated compound is solid at reaction temperature, the nitration rate depends in the first place on the concentration of the compound in acid, on the interfacial area and on the rate of diffusion of the acid into the solid phase. Of course, the interfacial area depends above all on the mixing of the two phases. Moreover, attention must be paid to the statement, first expressed by Hetherington and Masson [84], that the nitration reaction proceeds solely in the acid phase, especially when solid substances are nitrated.

In the light of the present state of knowledge on the problem it is more exact to say that the nitration reaction proceeds principally in the acid phase.

Consequently, mixing during nitration strongly affects the nitration result: vigorous stirring increases the nitration rate. This will be dealt with on pp. 266 and 314.

The favourable effect of strong dispersion on the nitration process can also be observed in nitration of easily emulsifiable substances. For example, Kobe and Doumani [94] found that commercial *p*- cymene can be nitrated more readily, than pure cymene, and this can be explained by the fact that the former of the two compounds is more readily emulsified.

The extension of the interfacial area by emulsification explains Miyagawa's [95] observation that the nitration rate can be considerably increased by the action of ultrasonics on a reacting system. For example, nitration of *m*- xylene to trinitro-*m*- xylene, which generally takes 2 hr, takes only 30 min when ultrasonics are used. There is no evidence as yet whether and how ultrasonic waves effect group orientations.

Attempts have been made by Bennett and his co-workers [43,87] to analyse in more detail the kinetics of a two-phase reaction system. However, so far it has proved impossible in the absence of more detailed data on the concentrations in the two phases. Bennett only found that in the nitration of dinitrotoluene to trinitrotoluene the H_2O:H_2SO_4 ratio in the organic phase is much higher than that in the acid phase. The proportion of acid in the organic phase is only 5-10% (in relation to this phase).

It has also been found that for any nitric acid concentration, the nitration rate is nearly proportional to the molar excess of sulphuric acid as related to the water content of the nitrating mixture. The nitrating acid excess is a factor of special importance in esterification of alcohols ("O-nitration"),

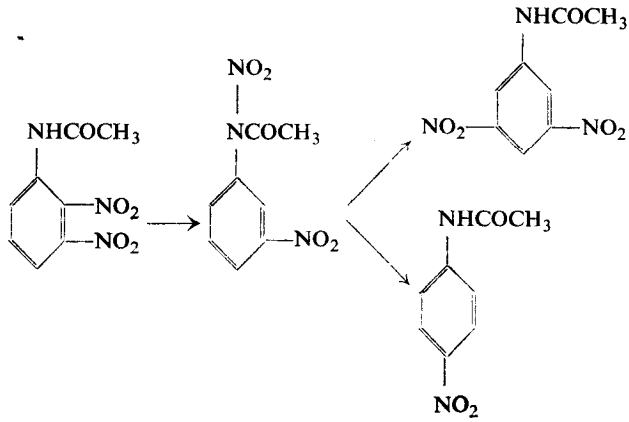
O-nitration of cellulose with mixtures of acids is a widely applied type of esterification reaction in a heterogeneous system. One of the factors influencing the reaction rate here is the rate of diffusion of the acid into the fibre.

The process of starch O-nitration by the Hackel and Urbanski's method (see Vol. II, Fig. 164) shows how homogeneity of the system affects the O-nitration grade.

Recently Pausacker and Scroggie [96] have suggested that the nitration re-

action may be reversible. Their assumption has been based on the observation that the heating of 2,3-dinitroacetanilide with sulphuric acid yields mainly 2,5-di nitroaniline (46% yield), 3,4-dinitroaniline (23% yield) and a small quantity of 2,3-dinitroaniline (5%).

However, more recent studies by these workers [97] show that the mechanism of these reactions consists in the reverse of the Bamberger rearrangement. It is known that the Bamberger rearrangement in aromatic nitramines consists in the nitro group wandering from nitrogen to carbon. The compounds studied by the authors would undergo reverse rearrangement, followed by the Bamberger rearrangement:



It has been found by the same authors that heating 2,3-dinitrophenol with sulphuric acid leads to partial isomerization to 2,5-dinitrophenol.

Other dinitro compounds, viz. those substituted in the 2,5- and 3,4-positions, do not undergo such rearrangement. This fact is evidence that only that group can migrate which meets with steric hindrance (i.e. the nitro group in the ortho position to the adjacent group or groups).

No evidence of reversibility of aromatic C-nitration has so far been found.

Thus T. Urbanski and Ostrowski [98] have kept solutions of various nitro derivatives of toluene in cont. sulphuric acid at 90-95°C for ca. 60 hr. *o*- Nitrotoluene (I), *m*- nitrotoluene (II), *p*- nitrotoluene (III), 2,4,6-trinitrotoluene (IV) and 2,4,5-trinitrotoluene (V) were examined. No appreciable change was found of the boiling points of (I) and (II), and of the melting points of (III)-(V). Only in the case of *m*- nitrotoluene and 2,4,5-trinitrotoluene the solution gave a very slight blue colour with diphenylamine. This might have been produced by trace splitting of the mobile *m*- nitro group and could not be considered as any evidence of an equilibrium in the systems examined.

Nitric acid and sulphur dioxide

Varma and Kulkarni [99] studied the nitrating action of nitric acid saturated with SO_2. This solution acts much more vigorously than the usual nitrating mixture

of nitric and sulphuric acids. Thus, phenol undergoes violent reaction and carbonization with HNO_3+SO_2. According to these workers aniline, methyl- and dimethylaniline also react with the mixture with an almost explosive violence to yield carbonized products. Because of the vigour of the reaction there are hardly any prospects of the practical use of the mixture. On the contrary, it seems that in many cases (nitration of phenols and aromatic amines) the presence of SO_2 in nitrating mixtures may be undesirable and even dangerous.

Nitric acid and fluorine compounds

It has been shown that the addition of sulphuric acid to nitric acid is not the sole method of producing an intensification of the nitrating properties of nitric acid. The addition of such substances as boron fluoride (R. T. Thomas *et al. [46])* or hydrofluoride (Simons *at al.* [47]) to nitric acid produces a similar effect.

These phenomena can also be explained by the formation of the nitronium ion, according to eqns. (28) and (29) (p. 16).

Nitric acid and perchloric acid

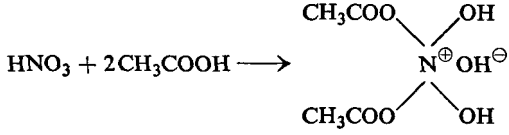
Nitration can also be carried out by solutions of nitric acid with perchloric acid [99a].

Bonner and Frizel [99b] describe O-nitration of isoamyl alcohol with a solution composed of fuming nitric acid (or N_2O_4) and perchloric acid of 55-62% $HClO_4$.

Nitric acid and acetic acid or anhydride

Acetic anhydride creates dehydrating conditions, therefore a mixture of nitric acid with acetic anhydride has strong nitrating properties. Moreover in esterification with nitric acid, the acetic acid present in the mixture or formed in the reaction does not hydrolyse the nitric acid ester formed.

Nitric and acetic acids. According to A. Pictet and Genequand [100], acetic acid combines with nitric acid (d = 1.52) to give a kind of mixed orthonitric and acetic anhydride, the so-called diacetylorthonitric acid (b. p. 127.7°C):



(47)

The same compound is formed when acetic anhydride and nitric acid ***(d*** = 1.4) are mixed.

However, no research work on the structure of the compound has been carried out yet. In particular there is no evidence to decide whether diacetylorthonitric acid is a true chemical compound or only an azeotrope.

Only recently Miskidzhian and Trifonov and their co-workers [101] examined the physico-chemical properties of solutions of nitric acid in acetic acid, such as the freezing point, viscosity, density, refraction, surface tension, electrical conductivity and heat of mixing. These authors came to the conclusion that nitric and acetic acids combine, yielding an addition compound $HNO_3.CH_3COOH$. The existence of Pictet's compound has not been verified.

Confirmation of these conclusions was provided in 1954 by Titov [35] who has studied the corrosion of steel in solutions of nitric acid in acetic acid. He found that the solution having the composition $HNO_3.CH_3COOH$ was the least corrosive.

Shatenshtein [102] drew attention to the fact that nitric acid in anhydrous acetic acid was much less dissociated than when in water, and that this could be explained by the protolytic properties of the solution components and by the low dielectric constant of acetic acid.

Recently Mint and Kecki [103] examined the Raman spectra of solutions of nitric acid in anhydrous and hydrated acetic acid. They have shown that at a concentration of 2 moles HNO_3 per litre of CH_3COOH, i.e. for the solution containing 12.6% HNO_3 in acetic acid, the 1304 cm^{-1} line, probably corresponding to the nitronium ion, NO_2^+, can be seen. The intensity of the line increases with concentration of nitric acid. Thus we can say that the acetic acid facilitates the formation of the nitronium ion.

The objective of Usanovich's work, mentioned above [50] was to elucidate the structure of mixtures of nitric acid with acetic or chloroacetic acid by means of conductometric measurements.

When studying the kinetics of the nitration reaction of phenol with nitric acid in the presence of acetic acid Briner and Bolle [104] found that the rate of nitration with this solution was higher than that with nitric acid of the same concentration.

A comparative study has also been made of the Raman spectra of the systems:

HNO_3-H_2SO_4-H_2O

HNO_3-$HClO_4$-H_2O

HNO_3-CH_3COOH-H_2O

by Mint, Kecki and Osiecki [105]. This led them to a conclusion that an increase of the acidity of the medium not only caused the dissociation of nitric acid to diminish, but also the Raman quantum efficiency of the 1300 cm^{-1} line to rise. This line corresponds to vibrations of the undissociated HNO_3 molecule. This in turn would indicate that the level of polarity of the bonds between the nitrogen and oxygen atoms of the NO_2 group was decreased as a result of the influence the medium exerts on the $HONO_2$ molecule. This would lead to an increase in the polarity of the bond between the NO_2 and OH groups and hence a weakening of this bond.

The authors express the view that the undissociated HNO_3 molecule is the nitrating agent in the solution HNO_3 - CH_3COOH-H_2O. The reactivity of the molecule is increased as a result of the polarized and weakened HO-NO_2 bond.

In 1950 Ingold, Hughes and Reed [39], when studying the kinetics of nitration with nitric acid in the presence of acetic acid, found the reaction to be of zero order in the case of aromatic compounds which are readily nitrated (benzene and its homologues), and its rate V_a could be expressed by the approximate equation:

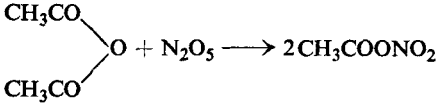
$$V_a = k_0 \text{ at } [HNO_3] = \text{const.}$$

While in case of compounds more difficult to nitrate (di- and tri-chlorobenzenesj. the reaction is of the first order and its rate V'_a may be expressed by the equation :

$$V'_a = k_1 [ArH] \text{ at } [HNO_3] = \text{const.}$$

According to the authors, the nitronium ion is the main nitrating agent in the presence of acetic acid.

Nitric acid and acetic anhydride. In their further work in 1907 Pictet and Khotinsky [106] found that acetic anhydride formed acetyl nitrate with N_2O_5:



(48)

Cohen and Wibaut [107] found when studying the kinetics of interaction of nitric acid and acetic anhydride, that after mixing the two substances, free nitric acid was present in the mixture during the first 75-100 min, then the HNO_3 concentration decreased in consequence of the reaction:

$$HNO_3 + (CH_3CO)_2O \text{ <-> } CH_3CONO_3 + CH_3COOH \quad (49)$$

The reaction did not stop at this stage but proceeded further since the nitrating action of acetyl nitrate on acetic anhydride yielded acetic nitroanhydride and consequently the concentration of acetyl nitrate decreased.

According to Cohen and Wibaut, it was nitric acid which was the nitrating agent at the beginning and later acetyl nitrate took its place.

Konovalov [108] observed an important fact as long ago as 1895. He reported that aromatic hydrocarbons with side chains were nitrated with this mixture chiefly in the side chain. Shorygin and Sokolova [109] confirmed this observation in 1930.

The kinetics of nitration of aromatic hydrocarbons with nitric acid in the presence of acetic anhydride was first studied by Tronov, Kamay and Kovalenko [110]. Their studies will be discussed later.

Menke [2] inferred from the results of his studies on nitration of aromatic hydrocarbons with mixtures of nitric acid and acetic anhydride that the latter acted not only as a dehydrating substance but also as a catalyst.

Recently Paul [111] examined kinetics of the nitration of benzene using solutions of nitric acid in acetic anhydride and acetic acid at 25°C. In a number of his experiments he also added sulphuric acid in a small quantity (ca. 0.01 M).

The results favour nitronium ion attack on benzene as the rate-determining step:

$$HNO_3 + H^+ \text{ <-> } H_2NO_3^+ \quad \text{(a)}$$

$$H_2NO_3^+ + (CH_3CO)_2O \leftrightarrow NO_2^+ + 2CH_3COOH \quad \text{(b)}$$

$$NO_2^{\oplus} + C_6H_6 \rightleftharpoons C_6H_5(H^{\oplus})(NO_2) \quad \text{(slow)} \quad \text{(c)}$$

Such a mechanism accounts for the first-order dependence of the rate on reaction the nitric acid concentration in presence of sulphuric acid.

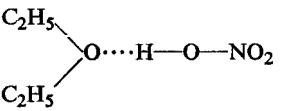
A higher-order dependence on nitric acid concentration in the absence of added strong acid (H_2SO_4) was also observed. This, according to Paul, is a consequence of the dual role assumed by nitric acid itself providing the proton acquired in step (a). The nitric acid-acetic anhydride reaction is not a simple one, and requires more study.

Nitration with mixtures of metal nitrates and acetic anhydride (or acid) was studied by Menke, and later by Spiegel and Haymann [112] and Bacharach [113]. It has been shown that only the nitrates which readily hydrolyse, such as ferric, nickel, cobalt, aluminium nitrates, have nitrating properties.

Solutions of nitric acid in organic solvents

Nitric acid in organic solvents does not produce the 1050 and 1400 cm^{-1} lines. On examination of absorption spectra in the infra-red, the conclusion has been drawn that nitric acid in chloroform or carbon tetrachloride solutions is less associated than when in a sulphuric acid solution (Dalmon [8,9,49]).

It follows from these investigations by Dalmon, that in an ether solution the nitric acid molecule probably combines with the ether molecule by means of a hydrogen bond:



Calorimetric measurements by Hantzsch and Karve [22] have shown that the heat of dilution of nitric acid with ethyl ether is higher than that with water. Hantzsch therefore suggested that nitric acid forms a compound with ether (probably through the hydrogen bond) as above. Dioxane also forms a similar compound with nitric acid.

Measurements of the vapour pressures of solutions of nitric acid in ether carried out by Dalmon and his co-workers confirmed the existence of the compound. It was shown that the vapour pressure of ether, which at 0°C was 185 mm Hg, decreased on addition of nitric acid and attained 1 mm Hg when equimolar proportions of the two components were present in the solution.

Ingold, Hughes and Reed [39] have studied the kinetics of nitration with nitric acid in the presence of nitromethane and found the reaction to be of zero order in the case of readily nitrated aromatic compound, and of first order with compounds

more difficult to nitrate as in the presence of acetic acid. Here also it was probably the nitronium ion that was responsible for nitration.

Nitric acid salts in mixtures with other acids

In the days when anhydrous nitric acid was not easily available, nitric acid salts ($NaNO_3$, KNO_3) mixed with sulphuric acid were widely used for nitration. Such mixtures acted similarly to the mixture of nitric and sulphuric acids. Later, as synthetic nitric acid became one of the most readily available chemical products, and the production of nitric acid salts from nitric acid had started, nitrating mixtures with sodium or potassium nitrates were abandoned. This is the principal explanation for the scarcity of investigations on the structure and action of such mixtures. It is believed that in such mixtures the nitronium ions are present, according to the equation :

$$NaNO_3 + 2H_2SO_4, \rightarrow NO_2^+ + 2HSO_4 + Na^+ + H_2O \quad (50)$$

Ingold and his co-workers proved in 1950 [39] that on introducing the NO_3^- anion into nitric acid in the presence of acetic acid or nitromethane the reaction rate decreased, since the formation of the NO_2^+ ion was hindered by the NO_3^- ion:

$$2HNO_3 \leftrightarrow H_2NO_3^+ + NO_3^- \text{ (fast reaction)} \quad (51)$$

$$H_2NO_3^+ \leftrightarrow NO_2^+ + H_2O \text{ (slow reaction)} \quad (52)$$

The nitration reaction rate depends on the kind nature of the cation. Mixtures of nitric and sulphuric acids nitrate the most slowly, and lithium nitrate acts the most rapidly. With regard to activity cations may be ranged in the following way:

$$H < NH_4 < K < Na < Ag < Li$$

This order also corresponds to the ease of conversion of bisulphates into pyrosulphates, which for the order presented is the highest for lithium salts (Klemenc and Schöller [34], K. Lauer and Oda [32], Lantz [83]).

Ceorgievskii [114] found that the yield of a nitration reaction also depends on the nature of the cation. For example, when benzene was nitrated to nitrobenzene, the best results were obtained with copper nitrate and sulphuric acid.

Fredenhagen [121] developed a method sometimes referred to as “Fredenhagen nitration” [122]. The nitrating agent consists of a nitrate, e.g. potassium nitrate in anhydrous or highly concentrated hydrogen fluoride.

Metal nitrates in the presence of Friedel-Crafts catalysts

Apart from the investigations on nitration with the nitrates of some metals in the presence of sulphuric or nitric acid Topchiyev [115] has carried out extensive studies on nitration with metal nitrates in the presence of $AlCl_3$, $FeCl_3$, $SiCl_4$, and BF_3. He showed that all the nitrates had nitrating properties, and he ordered the nitrates he studied according to their increasing nitration activity in the presence of $AlCl_3$:

$$Ba < Pb < NH_4 < Na < K < Ag$$

With KNO_3 and $NaNO_3$ the yield of nitrobenzene was 70 and 73% respectively, calculated on benzene.

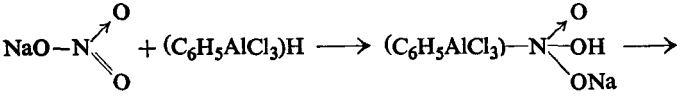
$AlCl_3$ and BF_3 were shown to be the most efficient catalysts, $FeCl_3$ was less efficient and the efficiency of $SiCl_4$ was the lowest.

The best yield of this nitration reaction is obtained at room temperature and in the presence of an excess of the aromatic hydrocarbon. An interesting feature of this nitration is that it is not accompanied by any oxidation processes. The method may find practical applications.

Topchiev has suggested the following hypothesis concerning the mechanism of nitration with nitrates in the presence of $AlCl_3$ or BF_3. Benzene is activated by aluminium chloride to give an addition product, according to the equation:

$$C_6H_6 + AlCl_3 \rightarrow (C_6H_5AlCl_3)H \qquad (53a)$$

The product reacts with sodium nitrate, yielding another addition product which decomposes to give nitro compound:



$$\rightarrow C_6H_5NO_2 + NaOH + AlCl_3 \qquad (53b)$$

CONCLUSIONS

It appears that concentrated nitric acid follows a heterolytic dissociation mainly according to the equation:

$$NO_2OH \leftrightarrow NO_2^+ + OH^-$$

The presence of acids stronger than HNO_3 accelerates the heterolysis of nitric acid into NO_2^+ and OH^-. It is for this reason that mixed acid is so effective:

$$HNO_3 + H_2SO_4 \leftrightarrow H_2NO_3^+ + HSO_4^-$$

$$H_2NO_3^+ + H_2SO_4 \leftrightarrow NO_2^+ + H_3O^+ + HSO_4^-$$

In neutral organic solvents (which do not react with the acids) only a second molecule of nitric acid can supply the necessary proton:

$$2HNO_3 \leftrightarrow H_2NO_3^+ + NO_3^-$$

$$H_2NO_3^+ \leftrightarrow NO_2^+ + H_2O$$

It should, however, be pointed out that most of the evidence presented by a number of authors, and chiefly by Ingold and his school in support of the nitronium ion mechanism of nitration, was obtained with homogeneous solutions under conditions that could not be compared directly with the conditions generally applied in industrial nitrations.

The work of Bennett and his co-workers [87] (discussed in detail on the p. 312) was an exception: a 50/50 mixture of di- and tri-nitrotoluene was nitrated by shaking with mixed acids of various compositions for a fixed time. The reaction was then quenched with cold water and the proportion of the dinitrotoluene which has been converted to trinitrotoluene was determined. The conversion, and the reaction rate, approach zero as the mole ratio water: sulphuric acid approaches unity. This is significant, because if this ratio considerably exceeds 1.0 the NO_2^+ ion is spectroscopically undetectable in sulphuric acid-nitric acid-water solutions. Bennett showed that various acid mixtures that gave the same conversion contained practically the same concentration of the NO_2^+ ion, as determined by Raman spectra. Hetherington and Masson [84] had already found that the reaction rate became negligibly small at certain concentrations and that a line drawn through the limiting boundary almost coincides with the boundary of the area of spectroscopic detection of NO_2^+ ions.

However, a few authors offered evidence showing that nitration can also occur with mixtures in which concentrations of the nitronium ion are too weak to be spectroscopically detectable (Lowen, Murray, Williams [116]; Bunton, Halevi, for C-nitration [93], and Urbanski and Hackel [80] for O-nitration). Also Brennecke and Kobe [117] drew attention to the experiments of McKinley and White [118] who found that the acids for mononitration lie outside the nitronium ion envelope.

All this created doubt as to whether the nitronium ion mechanism can be applied to all cases. As will be pointed out later, it seems that the mechanism of the nitration reaction is more complicated and may proceed under the influence of nitrating agents other than the NO_2^+ ion. According to Titov in his early work of 1941, nitration with nitric acid of moderate concentration (60-80% HNO_3) occurs through the action of NO_2 (or N_2O_4) and nitric acid plays only the role of a source of NO_2.

However, Bunton and Halevi [93] have expressed the view that the nitronium ion mechanism is still responsible for C-nitration even in highly aqueous conditions. Bunton, Halevi and Llewellyn [92] in their work described above (p. 38) examined the mechanism of oxygen exchange between nitric acid and water in an aqueous nitric acid medium by using isotopically labelled water. From the identity of the absolute rate of exchange in such a medium with the absolute rate in the same medium used for an aromatic nitration they suggested that the nitronium ion mechanism is responsible for nitration with nitric acid containing for example 60 mole % of water. Banner and Frizel [99b] have also suggested the nitronium ion mechanism for O-nitration of alcohols by nitric acid in aqueous solution.

It should be pointed out that phenols and anilides can be nitrated with very dilute nitric acid. The mechanism of such reactions might differ essentially from that of the reactions of C-nitration in other aromatic compounds, as it most likely passes through the formation of nitroso compounds which are then oxidized to the corresponding nitro compounds. This problem is discussed later (e.g. p. 85, 116).

Since industrial nitration occurs, in most cases, in two-phase system a number of workers have investigated the kinetics in both phases: organic and acid. Hetherington and Masson [84], McKinley and R. R. White [I18], Barduhn and Kobe [119] all reported that nitration of aromatic hydrocarbons takes place only in the acid phase. However, other workers (W. K. Lewis and Suen [120]) have shown, when nitrating benzene, that the reaction rate in the organic phase is an appreciable fraction (10-15%) of that in the acid phase.

As mentioned already (p. 40) it appears that nitration takes place mainly (but not exclusively) in the acid phase.

Taking into consideration that the rate of reaction in the organic phase is negligible compared with that in the acid phase, the following definition of the rate of nitration, R, of toluene in the unit volume of acid phase can be given

$$R = \frac{\text{moles of MNT produced}}{\text{hr x litre of acid phase}}$$

Brennecke and Kobe [117] reported that the rate of nitration of toluene appears to be proportional to the mole fraction of toluene in the effluent organic phase X_T (for acids containing not more than 30 mole % sulphuric and 15 mole % nitric acid). This suggested that the ratio $R:X_T$ is the rate that would be obtained if the organic phase were pure toluene. Kobe came to the conclusion that the mechanism of nitration through the nitronium ion controls the rate of reaction in acids containing more than 30 mole % of sulphuric acid.

The fact that most industrial nitrations take place in a two-phase system necessitated investigations into the influence of mixing on the rate of reaction.

A few authors, e.g. Kobe and his co-workers [117, 119], Orlova [123] have found that the rate of nitration greatly depends on the intensity of agitation of a reacting mixture. This is discussed in a more detailed way in the chapter devoted to the practical principles of nitration, i.e. the technology of the process and apparatus for nitration (pp. 152, 266, 288, 314).

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CHAPTER II

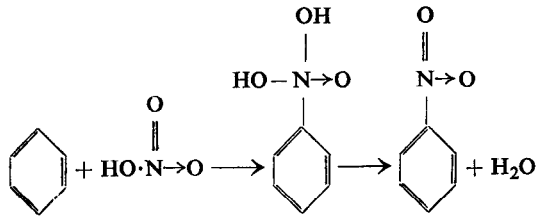
NITRATION THEORIES

THERE are two main theories concerning the nitration of hydrocarbons by means of the nitrating agents described above.

The first theory assumes a two-stage reaction with an addition reaction as the first stage and the second assumes that nitration is a double exchange reaction. At present the second theory has more adherents, since it is based on more recent experimental data.

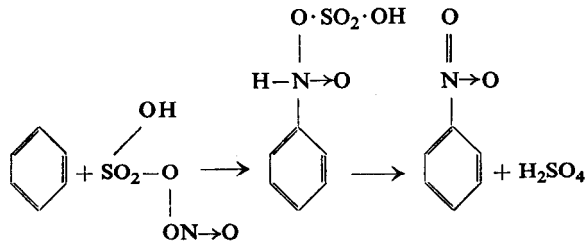
NITRATION AS AN ADDITION REACTION

According to Michael [l], on nitrating aromatic hydrocarbons an intermediate addition product is formed, which has one hydrocarbon hydrogen atom attached to one oxygen atom of nitric acid, and a carbon atom of the aromatic ring directly attached to the nitrogen atom of the acid. The "aldol" formed gives off water in the presence of an excess of nitric or sulphuric acid. The mechanism was depicted by the author as follows:



(1)

Likewise the mechanism of nitration of an aromatic hydrocarbon with nitrosulphuric acid $SO_2\langle^{OH}_{ONO_2}$ was formulated by Michael as:

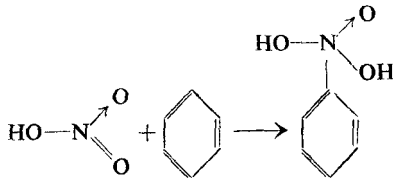


(2)

Here it is not water but sulphuric acid which is given off.

This view Michael confirmed in 1935 when he emphasized [2] that in a molecule of nitric acid the dominating factor, which facilitated the reaction, was the affinity of oxygen for hydrogen and of nitrogen for the aryl group.

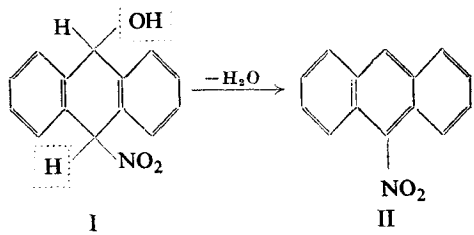
Hence the facility of the transformation:



(3)

However, Giersbach and Kessler [3] supposed that the initial step in the nitration reaction was the addition of two nitric acid molecules to a benzene molecule,

Experimental evidence of the possibility of the formation of products from aromatic hydrocarbons by the addition of nitric acid was provided by Meisenheimer [4]. He found that with anthracene the nitric acid molecule attached itself to the 9 and 10 carbons (of aliphatic character), yielding the product I, which in the presence of sodium hydroxide or acetic anhydride gave off water to form *meso*-nitroanthracene (II) :

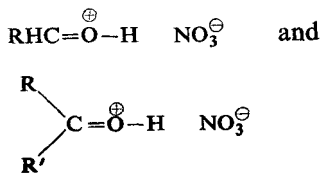


(4)

It has also been found that certain aldehydes, ketones and carboxylic acids esters form well defined products with nitric acid (Reddelien [5]). For example, bemzaldehyde with 60% nitric acid gives a colourless, unstable oil, and cinnamic aldehyde forms fairly stable white crystals, melting at 60-61°C, with 65% nitric acid. Acetophenone, benzophenone, fluorenone, phenanthrenoquinone and camphor give similar addition products.

They are converted to nitro compounds under the influence of nitric acid or acetic anhydride and are decomposed by water to give the initial components.

According to T. Urbanski and Hofman [5a] the ionic oxonium salt structure can be attributed to these compounds:



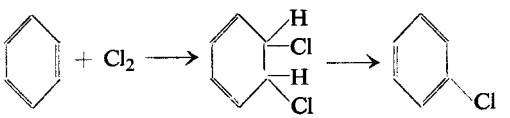
This was based on infra-red absorption spectra which show frequencies of the oxonium ion bond (O^+-H, ca. 2600 cm^{-1}) and of the nitrate ion.

Houben [6] gives the following sequence of transformations for "benzaldehyde nitrate" :

$$C_6H_5CHO.HNO_3 \begin{cases} + H_2O \rightarrow C_6H_5CHO + HNO_3 & (a) \\ \text{left in a hermetic vessel} \rightarrow C_6H_5COOH + HNO_2 & (b) \\ + (CH_3CO)_2O \rightarrow C_6H_5CH(OOC.CH_3)_2 + HNO_3 & (c) \\ + H_2SO_4 \rightarrow m\text{-}\ C_6H_4(NO_2)CHO + H_2O & (d) \\ + H_2SO_4 + (CH_3CO)_2O \rightarrow p\text{-}\ C_6H_5(NO_2)CHO + H_2O & (e) \\ + C_{10}H_8 \rightarrow C_6H_5CHO + C_{10}H_7.NO_3 & (f) \end{cases}$$

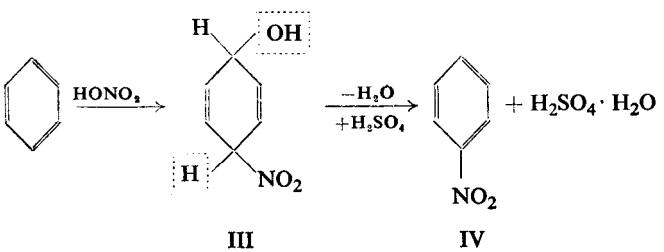
An interesting point is the influence of the compounds which react with an addition compound (reactions d and f) on the position of the nitro group introduced.

Following Thiele's view [7] that any aromatic substitution is preceded by the formation of an addition product Holleman [8] suggested in 1910 that the reaction of nitration, like that of chlorination, consisted in addition, followed by splitting off, according to the following scheme for chlorination:



(5)

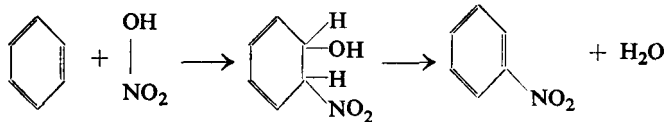
A similar scheme for the nitration process was given by Reddelien [5] who expressed the view that nitration of aromatic hydrocarbons with mixtures of nitric and sulphuric acids gave addition products, e.g.



(6)

The product (III) undergoes decomposition, the group OH being attached to H_2SO_4 as H_2O (IV). The addition product is hydrolysed by water, and mono- or polynitro compounds are formed.

Mainly on the basis of Holleman's hypothesis and studies on the nitration of olefins, Wieland [9,10] assumed the addition of a nitric acid molecule to the double bond, resulting in the formation of a cyclohexadiene derivative (V), followed by the loss of a water molecule:

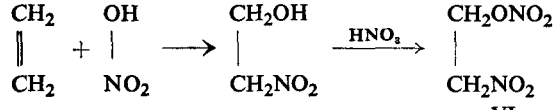


(7)

V

The addition of a nitric acid molecule to the double bond was first studied by Kekulé [11], who obtained an oily, explosive product on treating ethylene with concentrated nitric acid. Wieland [9,10] and Anschütz [12] believed the reaction to proceed principally according to the eqns. (8) and (9).

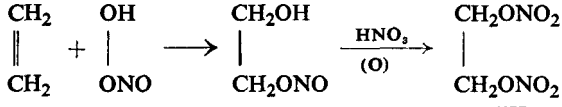
In support of this theory Wieland [10] reported the results of his investigations, carried out in co-operation with Sakellarios, where two products (VI) and (VII) were obtained in the reaction of ethylene with nitric acid:



(8)

VI

Nitroethyl nitrate



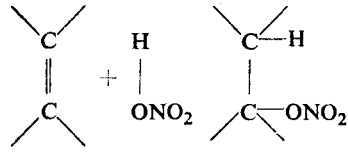
(9)

VII

Glycol dinitrate

In both reactions products were formed which resulted from addition (in the first stage of the reaction) of a nitric acid molecule to the double bond.

Wieland's theory was criticized. Michael and Carlson [2] called in question Wieland's view and proposed a different mechanism:



(10)

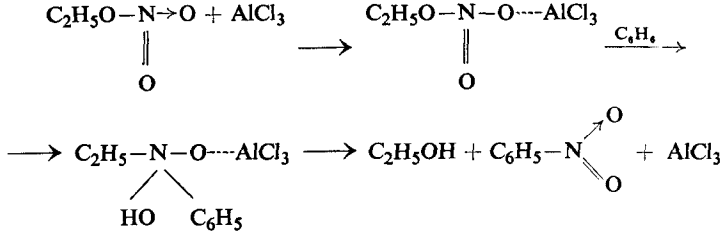
since they found that at temperatures below 0°C concentrated nitric acid adds to olefines, such as isobutylene, trimethylethylene, to yield the nitric esters of the corresponding alcohols. Other objections to the Wieland theory were also put forward by Topchiyev [13]:

(1) The cyclohexadiene derivative (V), formed by addition of a nitric acid molecule, is very unstable and it is difficult to speak about a definite direction of the decomposition reaction of the compound V.

(2) Against the theory of the similarity of the processes of attaching HNO_3 and Br_2 to the double bond is the fact that molecules are attached with different rate. Bromine is attached only with great difficulty (without a catalyst). On the contrary, nitration is very easy to carry out.

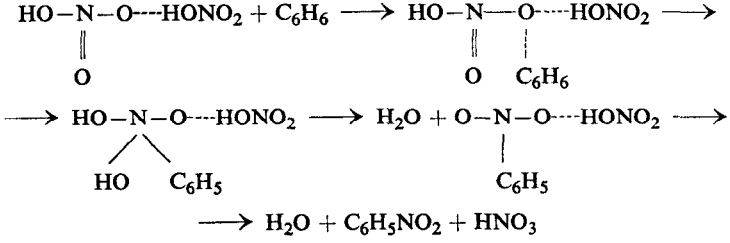
Taking this into account, Tronov [14,15,16] and Nametkin and Zabrodina [16a] advanced another idea, similar to Michael's initial hypothesis. Thus on the basis of Giersbach and Kessler's [16b] experiments Tronov inferred that one of the two HNO_3 molecules reacting with one molecule of benzene acts as a catalyst.

On the basis of Boedtker's experiments [17], who found that benzene was nitrated by ethyl nitrate in the presence of aluminium chloride, Tronov suggested the following mechanism for this process:



(11)

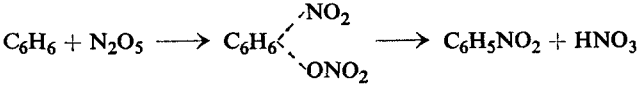
By analogy with this, Tronov gives the following plan for the general mechanism of nitration:



(12)

According to Schaarschmidt [18] the mechanism of nitration with a mixture of nitric and sulphuric acids consists in the formation of nitric anhydride which becomes attached to the aromatic compound. The addition compound is unstable and decomposes, giving a nitro compound and nitric acid. The mechanism of nitration suggested by Schaarschmidt is:

$$2HNO_3 + H_2SO_4 \leftrightarrow N_2O_5 + H_2SO_4.H_2O \qquad (13)$$



Unstable nitration product

Hetherington and Masson [19] suggested that nitrobenzene can form complexes with H_2SO_4 and HNO_3 and that the cation, $C_6H_5NO_2H^+$, of these complexes reacts with HNO_3 to form dinitrobenzene:

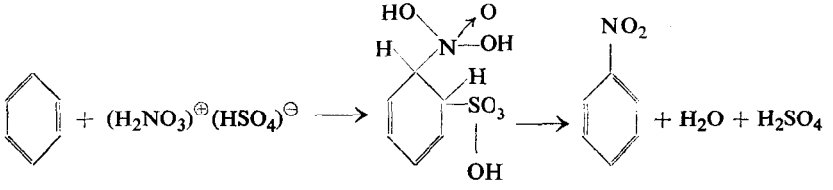
$$H_2SO_4 + C_6H_5NO_2 \leftrightarrow C_6H_5NO_2H^+ + HSO_4^- \qquad (14)$$

$$HNO_3 + C_6H_5NO_2 \leftrightarrow C_6H_5NO_2H^+ + NO_3^- \qquad (14a)$$

$$C_6H_5NO_2H^+ + H_2O \leftrightarrow C_6H_5NO_2 + H_3O^+ \qquad (15)$$

$$C_6H_5NO_2H^+ + HNO_3 \leftrightarrow C_6(NO_2)_2 + H_3O^+ \qquad (15a)$$

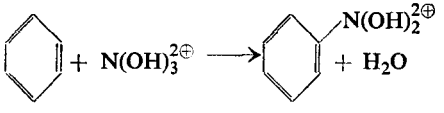
Lauer and Oda [20] assumed the existence of nitracidium sulphate (according to Hantzsch) and suggested that the mechanism of nitration with a nitrating mixture is as follows:



(16)

A similar nitration mechanism was suggested by Vorozhtsov [21]. He also assumed the formation of an addition product of the hydrocarbon with HNO_3 and H_2SO_4, followed by splitting off H_2SO_4 and H_2O.

Usanovich [22] also assumed Hantzsch's cations to be the nitrating agents in a mixture of nitric and sulphuric acids. He believed that in the nitration process the nitracidium cation was attached first accompanied by splitting off water:



(17)

On dilution with water the resulting new cation, $C_6H_5N(OH)_2^{2+}$, gives nitrobenzene:

$$C_6H_5NO_2H_2^{2+} + 2H_2O \rightarrow C_6H_5NO_2 + 2H_3O^+ \quad (18)$$

In the nitration of aliphatic hydrocarbons the NO_3^- ion reacts:

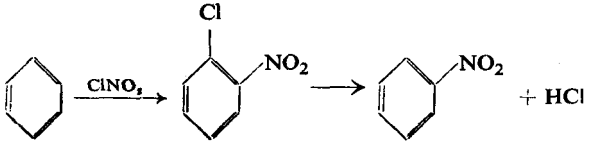
$$R.CH_3 + NO_3^- \leftrightarrow R.CH.NO_2(OH)^- \quad (19)$$

The anion formed may undergo a hydrolysis process in an acid medium:

$$R.CH_2NO_2(OH)^- + H_3O^+ \rightarrow R.CH_2NO_2 + 2H_2O \quad (20)$$

In favour of the view, that postulates the formation of an addition product during the first stage of nitration this fact should be known to all who are practically engaged in nitration of aromatic hydrocarbons. Immediately before contacting the nitrating acid (HNO_3 or nitric and sulphuric acids mixture), benzene and toluene give brown coloured products amid nitric acid vapours. On dissolution in the acid these products decolourize at once. It is quite possible they arc addition products formed by nitric acid vapours with the hydrocarbon.

The existence of similar addition products must be mentioned here. Steinkopf and Kühnel [23] observed that benzene reacted with nitryl chloride at room temperature under pressure to yield 1-chloro-2-nitrocyclohexadiene, which on heating released a molecule of hydrogen chloride giving nitrobenzene:



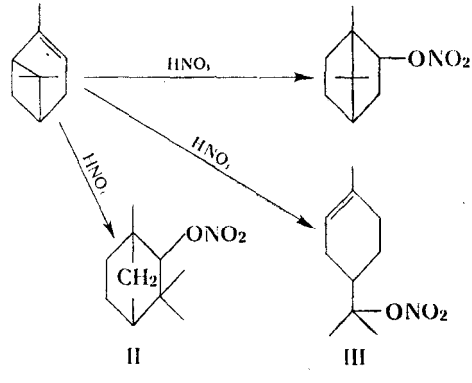
(21)

Thus, there is evidence that such addition is probable and it seems to confirm the basic scheme of Thiele-Holleman-Wieland, assuming that under certain conditions substitution with the NO_2 group may be preceded by the formation of addition products.

Although this view was replaced by the conception of the nitration reaction as double exchange reaction, it seems that the mechanism of the nitration reaction is rather a complicated one and under various conditions may proceed differently. The mechanism which includes addition may also exist, especially at low temperatures, and may not necessary proceed under the influence of the nitronium ion. It seems that nitric acid in the form of $HO\text{-}NO_2$ can be the nitrating agent acting through the addition mechanism.

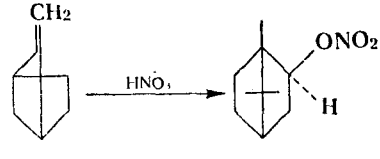
Studies of the nitration of terpenes are of interest too, as they provide evidence for the possibility of attaching a HNO_3 molecule to the double bond. Konovalov [24] obtained nitro derivatives from menthene, camphene, pinene and bornylene on acting with nitric acid. Bouveault [25] was able to prepare an addition product of camphene and HNO_3. He obtained an oily product with a structure that could not be well defined. The reaction of addition of nitric acid to the double bond was studied in detail by Sucharda [26]. He found that on acting on pinene with nitric acid containing 33% of KNO_3 instead of with pure nitric acid, or by introducing nitric acid vapours diluted with dry air, nitric acid esters were obtained in over 70% yield. When reduced with zinc dust in the presence of ammonia, the esters were converted to the corresponding alcohols.

Using both methods Sucharda obtained: borneol (I), fenchol (II) and terpineol (III) nitrates :



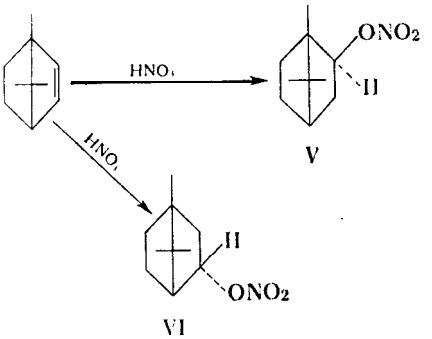
II III

H. Kuczynski and L. Kuczyliski [27] extended Sucharda's observations in their studies on other terpene hydrocarbons. They obtained isoborneol nitrate (IV) on reacting camphene with concentrated nitric acid (without KNO_3):



IV

From bornylene they obtained isoborneol (V) and epiborneol (VI) nitrates:

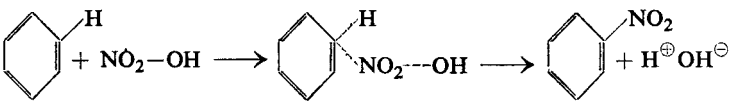


H. Kuczynski and L. Kuczynski have also studied the action of nitric acid on β– and δ– fenchene, limonene, sylvestrene and other terpene hydrocarbons.

It has also been shown that the addition of nitric acid molecules to olefins is not the only possible reaction of olefins with HNO_3. Formation of nitro-olefins, i.e. ordinary nitration by substitution, is also likely. This is discussed later (p. 81).

NITRATION AS A DOUBLE EXCHANGE REACTION

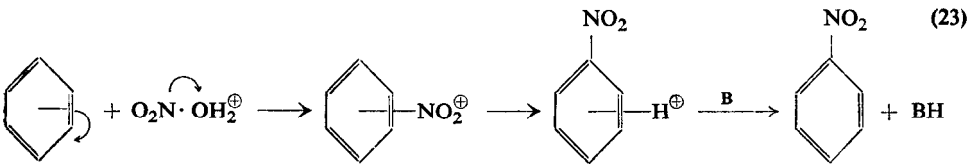
At present it is generally accepted that the nitration reaction is a double exchange reaction. The nitro group becomes attached to one of the carbons in an aromatic ring, while simultaneously an atom of hydrogen initially connected with an atom of carbon, is split off as a proton:



(22)

A nitration mechanism formula of this type was suggested by Ingold [28] in 1935.

In 1946, Dewar [29] gave the following mechanism for the double exchange with the nitracidium ion taking part:



(23)

B is a proton acceptor (e.g. the OH^- or HSO_4^- ions).

Benford and Ingold [30] pointed out in 1938 that the efficiency of bromination with a brominating agent of the general formula X-Br depended on the affinity of X for the electrons of the X-Br bond. It is known, for example, that Cl.Br is a better brominating agent than Br.Br. Likewise the efficiency of a nitrating agent, $X\text{-}NO_2$, depends on the affinity of X for electrons.

A still more powerful brominating agent is the free Br^+ ion, which is probably formed in the presence of ferric bromide used as a bromination catalyst:

$$FeBr_3 + Br_2 \rightarrow FeBr_4^- + Br^+$$

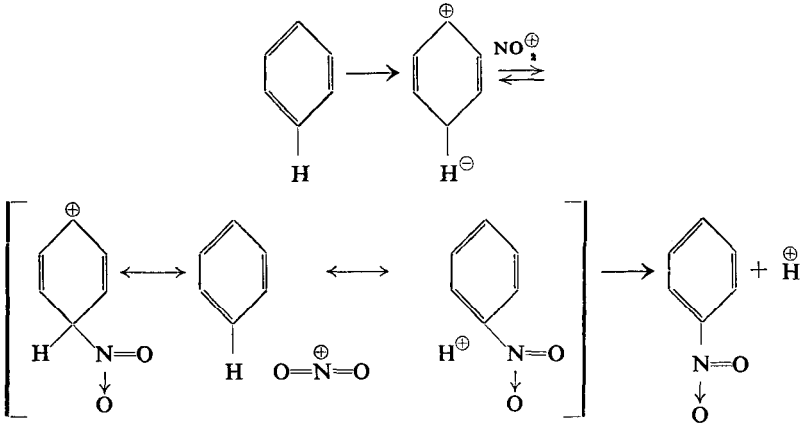
By analogy it is to be expected that the NO_2^+ is the most powerful nitrating agent.

Gillespie and Millen [31] arranged various nitrating agents according to increasing nitration power :

$C_2H_5O.NO_2$	ethyl nitrate
$HO.NO_2$	nitric acid
$CH_3COO.NO_2$	acetyl nitrate
$NO_3.NO_2$	nitric anhydride
$Cl.NO_2$	nitryl chloride
$H_2O.NO_2^+$	nitracidium ion
NO_2^+	nitronium ion

This order seems to require some alteration. For example, nitryl chloride has been found to be a definitely weaker nitrating agent than nitric acid and should have been placed before it.

On the basis of the numerous physico-chemical investigations referred to above, we assume that in the nitrating mixture HNO_3-H_2SO_4-H_2O the nitronium ion is present, it being the essential nitrating agent. Hence Titov [32] suggested in 1941 the following nitration mechanism where nitronium ion forms intermediate complex structures with aromatic compounds (in brackets):



(24)

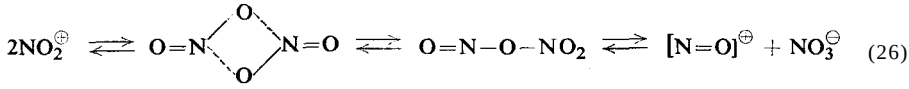
Ingold and his co-workers [33] and Bennett and co-workers [34-36] believed that the reaction rate depends on the concentration of the nitronium ions, NO_2^+. They suggested the following summarized nitration mechanism :

$$R.H + NO_2^+ + B \rightarrow R.NO_2 + HB \qquad (25)$$

where B is a proton acceptor, for example HSO_4^- or OH^- ions.

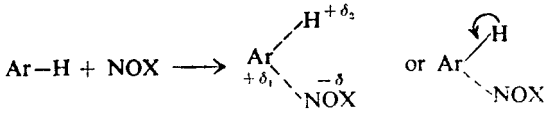
Or the basis of the results of his own experimental studies, Titov [37] in 1947 accepted this view, but at the same time he pointed out that the nitration reaction occurred in a more complex way than that suggested by Ingold. The nitrating agents

according to Titov were all the molecules and ions in equilibrium, viz.: NO_2^+, $NO\text{-}ONO_2$ and NO^+ :



(26)

These agents have both nitrating and nitrosating properties. Titov believed the nitration promoting energy was that generated by the transfer of electrons from the aromatic compound to nitrogen atoms of a nitrating or nitrosating agent according to the general formula NOX:



(27)

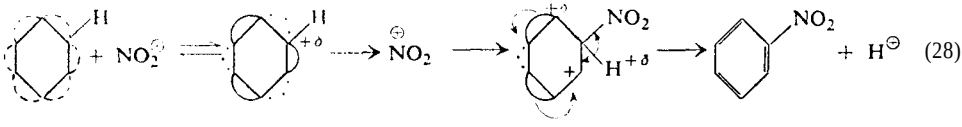
The difference in the electron affinities, ΔE, approximately equal to $k\delta$, necessary for the formation of the intermediate complex, depends to a great extent on the degree of steric accessibility and coordinative unsaturation of the nitrating and nitrosating agents.

Since according to the experimental data, the coordination number of nitrogen in its oxygen compounds does not exceed 3, the nitrogen atom in the nitric acid molecule is coordinatively saturated and has only slight electrophilic reactivity. This, according to Titov, makes the formation of addition products of nitric acid with aromatic compounds difficult.

Contrary to this nitrogen compounds with the coordination number 1 or 2 (thus, NO_2^+, NO^+ ions and $ONONO_2$), may exhibit their electrophilic reactivities and combine with the corresponding nucleophilic atoms of aromatic compounds.

To make it clear that splitting off a proton has no bearing on the rate of nitration a mechanism should be presented where the nitration reaction proceeds in, two steps, as pointed out by Melander [38] (p. 37).

Dewar's diagram eqn. (23) (see p. 60) already gives this idea, the binding of the proton by the acceptor B being the second step reaction. Titov [39] suggested recently a scheme which would clearly show the step-wise mechanism:



(28)

Here aromatic bonds are designated with dotted curved lines. Plain curved lines are π– bonds, three dots signify weaker π– bonds (as in 2,3-butadiene), the dotted arrow (->) represents shifting of π– electrons into the cation field, and the curved arrow (↷) the displacement of electrons. These denote the most important forms of the conjugations.

According to Ingold nitration is the simplest form of electrophilic substitution.

Recently Ingold and his co-workers [40] summarized the results of their investigations [41-48] into the three forms of nitration: C-, O- and N- nitration. The nitronium ion is formed in two stages, the first of which (a) - protonation -is always fast:

$$HNO_3 + HNO_3 \leftrightarrow H_2NO_3^+ + NO_3^- \quad \text{(fast)} \qquad \text{(a)}$$

$$H_2NO_3^+ \leftrightarrow NO_2^+ + H_2O \quad \text{(slow)} \qquad \text{(b)}$$

$$NO_2^{\oplus} + ArH \longrightarrow Ar\begin{matrix}H^{\oplus}\\ \\ NO_2\end{matrix} \quad \text{(slow)} \qquad \text{(c)}$$

$$Ar\begin{matrix}H^{\oplus}\\ \\ NO_2\end{matrix} + NO_3^{\ominus} \longrightarrow ArNO_2 + HNO_3 \quad \text{(fast)} \qquad \text{(d)}$$

If O- or N- substitution takes place, the reactions (a) and (b) proceed in the same way. In O- nitration, the subsequent reactions take place according to the following scheme :

$$CH_3OH + NO_2^{\oplus} \longrightarrow CH_3\overset{\oplus}{O}\begin{matrix}NO_2\\ \\ H\end{matrix} \quad \text{(slow)} \qquad \text{(c')}$$

$$CH_3\overset{\oplus}{O}\begin{matrix}NO_2\\ \\ H\end{matrix} + NO_3^{\ominus} \longrightarrow CH_3ONO_2 + HNO_3 \quad \text{(fast)} \qquad \text{(d')}$$

Ingold gives the following examples of N-nitration reactions:

$$(NO_2)_3C_6H_2H\begin{matrix}H\\ \\ CH_3\end{matrix} + NO_2^{\oplus} \longrightarrow (NO_2)_3C_6H_2\overset{\oplus}{N}\begin{matrix}NO_2\\ -H\\ CH_3\end{matrix} \quad \text{(slow)} \qquad \text{(c")}$$

$$(NO_2)_3C_6H_2\overset{\oplus}{N}\begin{matrix}NO_2\\ -H\\ CH_3\end{matrix} + NO_3^{\ominus} \longrightarrow (NO_2)_3C_6H_2N\begin{matrix}NO_2\\ \\ CH_3\end{matrix} + HNO_3 \quad \text{(fast)} \qquad \text{(d")}$$

In all these diagrams splitting off the proton is the last stage of the reaction.

ORIENTATION OF NITRO GROUPS

The orientation of a nitro group entering an aromatic ring depends first of all on the substituent already present in the ring and to a lesser degree on the composition of the nitrating acids, the nitrating conditions, etc. It is well known that the nitro group itself directs substituents to the *meta* position.

The problem of the orientation of nitro groups is connected with that of nitration kinetics. Nitration kinetics have already been discussed in connection with the composition of nitrating mixtures, especially with regard to the presence and the role of nitronium and other ions in the nitration process. Now nitration

kinetics will be considered from another viewpoint-that of the influence of various substituents in promoting or inhibiting further substitution.

A great deal of research work has been carried out with the object of studying the orientation of nitro groups introduced into an aromatic ring. The most ex-

TABLE 2

Group present on the ring	Composition of the product		
	% ortho-	*% meta-*	*% para-*
F	12.4	trace	**87.6**
Cl	30.1	trace	**69.9**
Br	**37.6**	trace	**62.4**
I	**41.1**	trace	**58.7**
CH_3	**58.8**	**4.4**	**36.8**
CH_2Cl	**40.9**	**4.2**	**54.9**
$CHC1_2$	**23.3**	**38.8**	**42.9**
CCl_3	**6.8**	**64.5**	**28.7**
$COOC_2H_5$	**28.3**	**68.4**	**3.3**
COOH	**18.5**	**80.2**	1.3
NO_2	**6.4**	**93.2**	0.25

tensive investigations are those by Holleman [49-55], who in the period 1895-1924 carried out numerous experiments and systematized the data obtained.

Holleman [55] gives the following data on the composition of the nitration products obtained in the nitration of different monosubstituted benzene derivatives with mixtures of nitric and sulphuric acids (Table 2). As appears from the data shown below, the substituent already present affects the orientation of the group which is being introduced. It is evident that nitration can be influenced by the steric factor. For exampl: tert.-butylbenzene is mainly nitrated in *para* (72.7%) and to a much lesser extent in *ortho* (15.8%) positions (H. C. Brown and Nelson [88]).

TABLE 3

Temperature, °C	Composition of the product		
	% ortho-	% para-	% meta-
-30	55.6	41.7	2.7
0	56.0	40.9	3.1
+30	56.9	39.9	3.2
+60	57.5	38.5	4.0

The influence of the nitration temperature on the orientation of a nitro group is in certain cases rather marked. When nitrating toluene with a mixture of nitric and sulphuric acids at -5°C, Pictet [56] observed that more para-isomer was obtained than at the temperature of 0°C.

Holleman and Arend [49] gave more detailed data, showing the influence of temperature on the composition of the product obtained in the mononitration of toluene with a mixture of nitric and sulphuric acids (Table 3).

Similar results have been obtained in the nitration of chlorobenzene, as shown in Table 4.

TABLE 4

Temperature, °C	Composition of the product	
	% *ortho-*	% *para-*
0	30.1	69.9
-30	26.9	73.1

As for naphthalene, Pictet [56] found that nitration at temperatures from -50 to -60°C mostly resulted in the formation of 1,5-dinitronaphthalene with a certain amount of the 1,3-isomer, while at a temperature higher than room temperature 1,5-dinitronaphthalene is formed along with l,8-isomer.

Bradfield and B. Jones [57] applied the Arrhenius equation, known from chemical kinetics, to the reaction of substituting various benzene derivatives by the nitro group (or by chlorine) at different temperatures:

$$k = nA\exp\left(-\frac{E}{RT}\right)$$

where for each isomer:

k - rate constant for the substitution reaction,

E - activation energy,

A - coefficient independent of temperature,

T - absolute temperature,

R - gas constant,

n - number of equivalent substitutions possible (for example, in the conversion of a monosubstituted into an ortho-disubstituted derivative n = 2, into a meta-disubstituted derivative, n = 2, and into the para-disubstituted derivative n = 1).

The number of isomers formed in a substitution reaction at a given temperature may be calculated if the composition of the substitution product, obtained at a different temperature is known. The equations have to be worked out for each isomer, in which k_o, A_o, E_o, k_m, A_m, k_m, k_p, A_p, E_p are the values, corresponding to the *ortho-*, *meta-* and *para-* isomer respectively.

The procedure of Bradfield and B. Jones was applied later by W. W. Jones and Russel [58] to their experiments on the nitration of toluene (their work will be further discussed later on p. 274). The results they obtained established the rule: a lower nitration temperature causes an increase in the quantity of *para-* nitrotoluene formed and reduces the amounts of *ortho-* and *meta-* isomers.

The nature and composition of the nitrating agent distinctly affects the composition of the nitration products.

Noelting and Forel [59] stated that an increase in HNO_3 concentration in the nitrating mixture increases the amount of *para-* nitro compound produced. Thus,

for example, in nitrating toluene with a mixture of nitric and sulphuric acids they obtained a product containing 60% of *p*- nitrotoluene, while in nitration with nitric acid alone the *para*- isomer content was 66%.

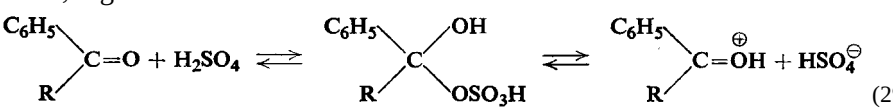
Baker and his co-workers [60,61] investigated the influence of the sulphuric acid concentration in nitrating mixtures on the *meta*- nitro derivatives of the following compounds: benzaldehyde, benzophenone and ethyl benzoate. The content of a *meta*- nitro derivative increases with the increase in acidity of the solution. For example, in nitration with a nitrating mixture contaming 80% sulphuric acid the yield of *m*- nitrobenzaldehyde is 83.9%. When nitrated with a mixture containing

TABLE 5

NITRATION OF ANILINE AND ANILIDES

Nitrated compound	Composition of the product		
	% *ortho*-	% *meta*-	% *para*-
With nitric acid			
Aniline nitrate	4	40	56
Acetanilide	42		58
Benzanilide	40		60
Formanilide	35	-	65
Chloroacetanilide	27	-	73
Oxanilide	15	-	85
	12	-	88
With a solution of 94% nitric acid in the concentrated sulphuric acid			
Aniline	1	49	50
Acetanilide	8	-	92
Benzanilide	7	-	93
Formanilide	6	-	94
Chloroacetanilide	4	-	96
Oxanilide	2	-	98
	2	-	98
With a solution of 80% nitric acid in anhydrous acetic acid			
Aniline	36	-	64
Acetanilide	30	-	70
Benzanilide	28	-	72
Formanilide	26	-	74
Chloroacetanilide	25	-	75
Oxanilide	21	-	79
	16	-	84

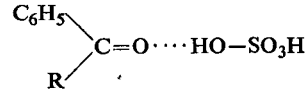
oleum (7.3% of free SO_3), benzaldehyde gives *m*- nitrobenzaldehyde in 90.8% yield. According to Baker, under the influence of sulphuric acid, the oxonium ion is formed, e.g.:



(29)

The oxonium group directs mostly to the *meta* position.

Gillespie and Millen [31] believed that sulphuric acid in an intermediate addition product is linked to the carbonyl group by a hydrogen bond:



K. Lauer [62] obtained the results (given in Table 5) by nitrating aniline and anilides with nitric and with mixtures of nitric and sulphuric or acetic acids at 20°C, over 24 hr.

It can be seen from the results referred to and also from the earlier data of Holleman and his co-workers [53] that aniline acylation has a decisive influence on the orientation of the nitro group.

When nitrating *p*- cresol, Holleman [51] found that according to whether *p*- cresol was reacted alone or as the *p*- cresol carbonic ester different isomers were obtained (Table 6).

TABLE 6

Nitrated compound	Composition of the product	
	% 2-nitro	% 3-nitro
p- Cresol	trace	close to 100
p- Cresyl carbonate	96.3	3.7

Holleman compared the data obtained by Pictet and Khotinsky [63] in the nitration of toluene with acetyl nitrate with those obtained by other authors in the nitration of toluene with a conventional nitrating mixture. The results are tabulated below (Table 7).

TABLE 7

Nitrating agent	Composition of the nitration product	
	% ***ortho-***	% ***para-***
Acetyl nitrate	88	12
Nitric and sulphuric acid mixture	55	40

Martinsen [64] in his studies on nitration kinetics determined the influence of substituents on the rate of the reaction. He classified them according to their influence on the reaction rate, comparing it with that of chlorine, which in some cases (as compared with hydrogen) can lower, while in others raise the rate:

$$\underset{\text{decreasing the reaction rate}}{NO_2 > SO_3H > COOH > Cl} < \underset{\text{increasing the reaction rate}}{CH_3 < OCH_3 < OC_2H_5 < OH}$$

It is interesting to know that the substituents which decrease the reaction rate direct towards the *meta* position while those increasing it direct towards the *ortho* and *para* positions.

The rule was checked by Tronov and Ber [15] when nitrating aromatic compounds with nitric acid in nitrobenzene. They found there was no simple correlation between the influence of a substituent on the reaction rate and its orienting activity. The rule is true only for the groups with strong orienting activity (e.g. NO_2, CN, CH_2CN, C_6H_5CO).

Ingold [65] gave the following order, representing activating properties of substituents in the nitration of an aromatic ring:

$$CH_3 > H > F, I > Cl, Br > COOC_2H_5 > SO_3H > NO_2$$

The introduction of several groups intensifies the action of the substituents. Thus Tronov and Ber have found that *o*-, *m*-, and *p*- xylene are nitrated 1.6-1.9, 4.5-4.9 and 5.7-10.5 times faster respectively than toluene. According to Ingold, *p*- dichlorobenzene is nitrated more slowly than chlorobenzene.

Striking data for the deactivating properties of nitro groups have been provided by Westheimer and Kharasch [65a]. They are related to the known fact that the nitration of nitrotoluene proceeds much faster than that of dinitrotoluene.

Tronov, Kamay and Kovalenko [66] have measured the rate of nitration of aromatic hydrocarbons and their halogenides with a mixture of nitric and acetic acids. The compounds examined were arranged according to increasing rate of nitration the relative rate is given in brackets, taking 1 for benzene:

$$C_6H_5Cl\ (0.15) < C_6H_5Br\ (0.25) < C_6H_5CH_2Cl\ (0.4) < m\text{-}\ CH_3C_6H_4Cl(0.5) < C_6H_6\ (1) <$$

$$< p\text{-}\ CH_3C_6H_4Cl(1.15) < o\text{-}\ CH_3H_4Cl(1.2) < m\text{-}\ \text{xylene}\ (7) < \text{mesitylene}\ (2.5)$$

If there are two substituents on the ring directing the NO_2 group into different positions more isomers may of course, be formed. Holleman [55] analysed minutely the problem as to which isomers were obtained in such cases. He established that their position, or positions, depend on the effect of separate groups on the reaction rate.

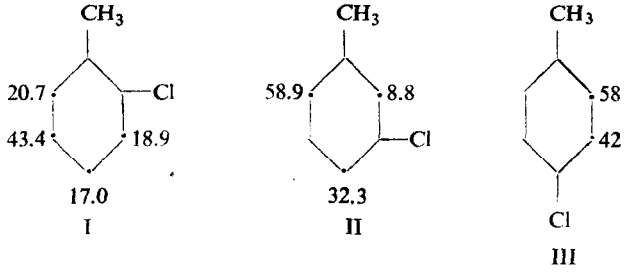
He arranged ***ortho-*** and *para-* orienting groups, according to their decreasing substitution rates, as follows :

$$OH > NH_2 > I > Br > CI > CH_3$$

and did likewise for meta-orienting groups:

$$COOH > SO_3H > NO_2$$

When nitrating aromatic compounds containing more than one substituent, the position of a new entrant group may be predicted from the number of isomers obtained by nitrating the compound with each of the substituents taken separately. Wibaut [67] studied this problem in detail when nitrating chlorotoluenes. He found that all possible isomers could be formed from *o*- chlorotoluene (formula I). The figures in different positions give the percentage of the corresponding isomers. By nitrating *m*- chlorotoluene, three isomers were obtained (II) and by nitrating *p*- chlorotoluene, two isomers (III):



From these data Wibaut calculated the ratio of the substitution rate influenced by the CH_3 and Cl groups to be:

$$CH_3 : Cl = 1 : 1.475$$

To obtain the ratio of nitration rates when the CH_3 or Cl group was present alone in a nitrated compound, Wibaut nitrated a mixture of toluene and chlorobenzene with only a small quantity of concentrated nitric acid. It was found that contrary to all expectations based on earlier observations, toluene was nitrated much faster than chlorobenzene. From this it must be concluded that the ratio of the nitration rates influenced by the two groups present together differed completely from that when only one of the groups was present in the ring.

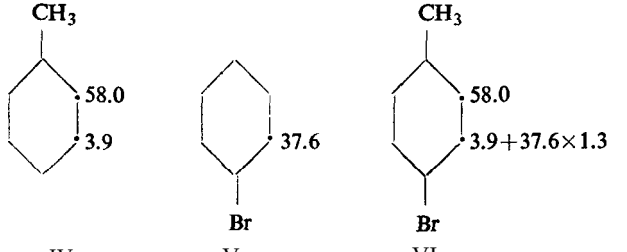
Taking that into account, Holleman [55] calculated which isomers were formed when nitrating bromotoluenes. These calculations were based on the following experimental data of his own:

(1) the ratio of the isomeric nitrotoluenes, resulting from the nitration of toluene,

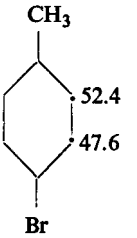
(2) the ratio of the isomeric bromonitrobenzenes, resulting from the nitration of bromobenzene,

(3) the ratio of the substitution rates influenced by the bromine and the methyl group present in the benzene ring simultaneously. This was calculated by Holleman from the ratios: Cl : Br = 1 : 0.88 (Holleman [54]) and CH_3 : Cl = 1 : 1.475 (given by Wibaut), from which he obtained CH_3 : Br = 1 : 1.3.

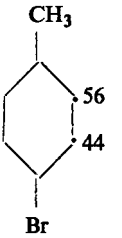
Since toluene, when nitrated, yields the ***ortho***- and *meta*- isomers in the quantities shown in diagram IV, and bromobenzene in those shown in diagram V, for *p*- bromotoluene the quantities can be calculated. They are shown in diagram VI.



The percentage is shown in diagram Via. Diagram VIb shows the values found experimentally. It can be seen that they differ only slightly from the calculated ones:



VIa

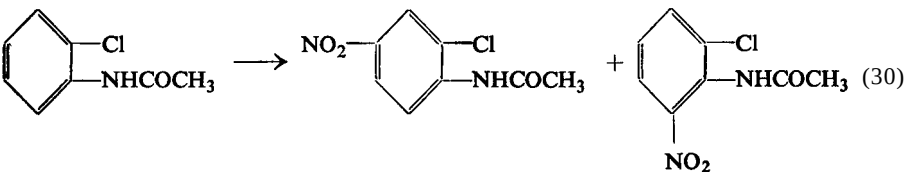


VIb

Holleman points out that such good agreement between the calculated and experimental values is not always the case. Moreover, instances are known of de viations from the substitution rules. According to Holleman [55] they may be ascribed in many instances to insufficient accuracy in the experimental data.

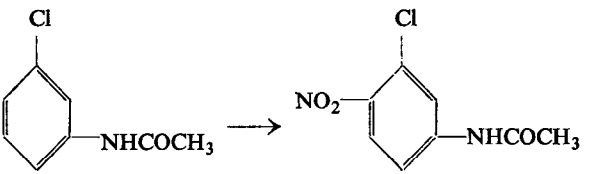
Marked deviations were observed when the nitro group was introduced into benzene derivatives with three substituents, e.g. into 2,3-dichloroacetanilide (Holleman and Hollander [52]).

Earlier Lobry de Bruyn [68] found that the nitration of *o*- and *m*- chloroacetanilides (VII) and (X) gave the products VIII, IX and XI, respectively:



(30)

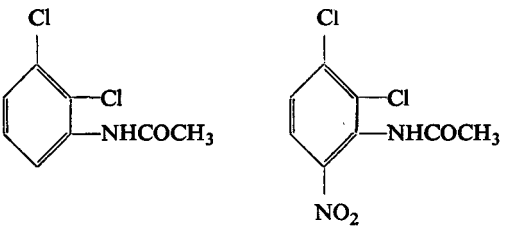
VII VIII 59% IX 39%



(31)

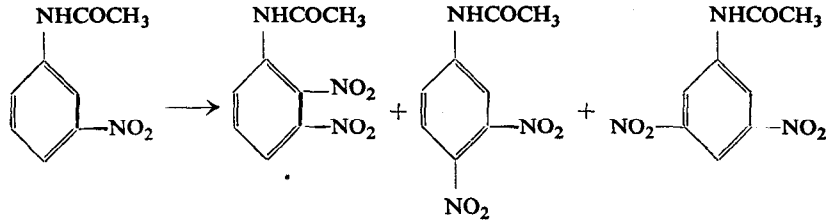
X XI 56%

From this Holleman inferred that in the nitration of dichloroacetanilide (XII) the nitro group should enter the 6- position, yet he obtained the substitution almost exclusively in 4- position (XIII)



XII XIII

Vorozhtsov [21] referred to the nitration of *m*- nitroacetanilide (XIV) as an example of inconsistency between the results obtained and predicted, viz.:

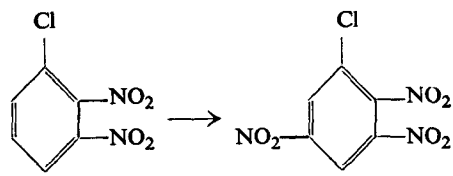


(32)

XIV XV 50% XVI 30% XVII 6%

A characteristic feature of the reaction is a complete lack of *meta* orientation to the nitro group. However, this is a rather complicated case of nitration accompanied by Bamberger rearrangement (p. 41 and Vol. III).

Holleman [47] also gave an example of an anomaly in the nitration of chloro-2,3-dinitrobenzene (XVIII). Instead of the third nitro group entering into the 4- or 6 positions as expected, which would be consistent with the orienting action of Cl and of one of the NO_2 groups, he obtained compound XIX, with the third nitro group in the 5- position:



(33)

XVIII XIX

Among more recent investigations the experiments of Hammond, Medic and Hedges [69] deserve special attention. They explain the influence of the medium on orientation when nitrating 2,5-dichloro- and 2,5-dibromo-nitrobenzene. Substitution into all three free positions takes place and derivatives *ortho-*, *meta-* and

TABLE 8
NITRATION OF 2,5-DICHLORONITROBENZENE

Nitration at 100°C with	*% ortho-*	*% meta-*	*% para-*
Fuming sulphuric acid and sodium nitrate (6%)	14.5	53.0	32.5
96.2% sulphuric acid and sodium nitrate (6%)	21.4	50.8	27.7
96.2% sulphuric acid and sodium nitrate (15%)	35.0	45.7	19.3
Nitric acid and 60% perchloric acid (2%)	33.1	45.1	21.1

para- to the nitro group are formed. The yield of the *ortho-* derivative may vary from 11.0 to 35.0% while of the yield the *meta-* derivative amounts to 45.7%. The quantities of the different isomers depend on the nitrating agent. For example, in the nitration of 2,5-dichloronitrobenzene the results obtained have been shown in Table 8. The modern approach to substitution rules consists in molecular orbital calculations [89].

A number of authors have studied substitution with the nitro group in benzene derivatives containing *ortho-para* directing substituents, when nitric acid with acetic anhydride was used. The experiments led to the conclusion that replacement of water in the nitrating mixtures by acetic anhydride produces an increase of the ratio of *ortho-* to *para-* isomers.

This was observed in the nitration of acetanilide (Holleman, Hertogs and van der Linden [53]; Arnall [70]), propionanilide (Arnall [70]), anisol (Griffiths, Walkey and Watson [71]; Halverson and Melander [72]). The effect was much less pronounced when toluene was nitrated (Hollernan, Vermeulen and de Mooy [54]).

Recently Paul [73] nitrated chloro- and bromobenzene with a solution of nitric acid in acetic anhydride with the addition of a catalytic quantity of sulphuric acid. The result was contrary to that observed earlier: the proportion of *para-* isomer was much higher than in the instance of nitration with 90% nitric acid, e.g. acetic anhydride containing 2 M HNO_3 and 0.04 M H_2SO_4 nitrated chlorobenzene to yield o- and p-chloronitrobenzenes in the proportion of 10:90. When 90 per cent nitric acid was used alone Holleman and Bruyn [50] obtained the isomers in the proportion 30:70. Bromobenzene gave the figures 25:75 and 38:62 respectively. According to Paul, the result depends on dipole moments: (1) of substituents attached to the ring (prior to nitration) and (2) of the solvent (such as acetic anhydride).

TABLE 9

RELATIVE REACTIVITY TOWARDS NITRATION

Compound	Relative reactivity		
	ortho	***meta***	***para***
$C_6H_5.H$	1	1	1
$C_6H_5.CH_3$	43	3	55
$C_6H_5.COOC_2H_5$	0.0026	0.0079	0.0009
$C_6H_5.Cl$	0.030	0.000	0.139
$C_6H_5.Br$	0.037	0.000	0.106

Among other researches, those carried out by Ingold and his co-workers [74,75] are of considerable importance. They have determined the relative reactivities of the various *ortho, meta* and *para* positions in several substituted benzenes by competitive nitration. Relative rates of nitration were determined in experiments in which benzene and a substituted benzene derivative were nitrated together, an insufficient quantity of nitric acid being used. The relative quantities of the products: $C_6H_5NO_2$ and $X.C_6H_4.NO_2$ gave the relative rates of nitration of benzene and of $C_6H_5.X$. When these results were combined with the relative quantities of *o-*, *m-* and *p-* isomers formed, it was possible to arrive at figures representing the relative reactivity of each of the possible substitution positions (Table 9).

The results show that the methyl group is a typical *ortho-para* directing group. The relative reactivity of all three positions is greater than that of benzene. This

is in accordance with the known electron-repelling effect of the methyl group.

The ester group lowers the reactivity of all three positions, but especially that of the *ortho* and *para* positions, in accordance with the known electron-attracting effect of the group.

On the basis of these experiments, the conclusion could be drawn that nitration is not only an electrophilic reaction, but that the orientation of the product is controlled by the selective activation and deactivation of various substitution positions.

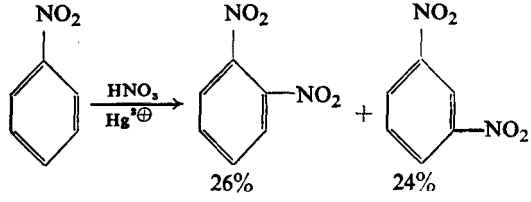
Ingold also examined the directing influence of a positively charged group $-N(CH_3)_3^+$. In nitration this group directs exclusively into the *meta* position. When, however, the positive charge is separated by $(CH_2)_n$ groups, the amount of *meta* substituted product rapidly diminishes as *n* increases. Thus:

$C_6H_5N(CH_3)_3$	100% *meta*-
$C_6H_5CH_2N(CH_3)_3$	88%
$C_6H_5CH_2N(CH_3)_3$	19%
$C_6H_5CH_2CH_2CH_2N(CH_3)_3$	5%

Similarly the ***meta***- directing force of the nitro group is rapidly diminished when it is separated from the ring:

$C_6H_5NO_2$	93% *meta*-
$C_6H_5CH_2NO_2$	67%
$C_6H_5CH_2CH_2NO_2$	13%

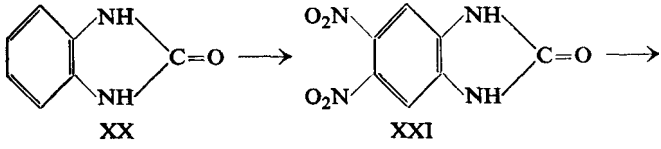
Ogata and Tsuchida [76] found in 1956 that the orienting activity of the nitro group may be partly changed in the presence of mercury ions. Thus, from nitrobenzene fairly considerable quantities of *o*- dinitrobenzene are obtained Blong with *m*- dinitrobenzene :



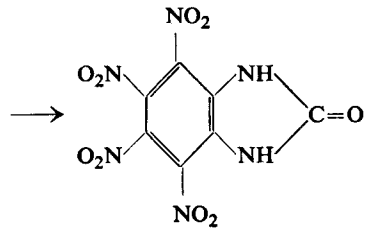
(34)

Other instances of anomalous substitution under the influence of substituents already present on the ring are also known.

Thus, for example, Kym and Ratner [77] found that benzimidazolone (XX) is readily nitrated to the 5,6-dinitro derivative (XXI). According to the experiments of Efros and Yeltsov [78] the compound obtained may undergo further nitration to the tetranitro derivative (XXII) having all nitro groups placed adjacent to one another (see also p. 552):



XXI



(35)

XXII

It should be borne in mind that since the advent of chromatography, it is now possible to separate and identify the constituents of complex mixtures which formerly presented some difficulty. It therefore seems desirable that some of the existing data on the composition of nitration products, particularly those obtained in earlier studies should be re-examined using up to date techniques.

Finally attention must be drawn to the fact that the orienting effect of the nitro group in nucleophile and radical reactions usually differs from that in electrophilic reactions, and instead of *meta* orientation, *ortho* or *para* orientation takes place. The corresponding observations are referred to in chapters dealing with nucleophile and radical substitutions of nitro compounds (pp. 204, 207 and 212 respectively).

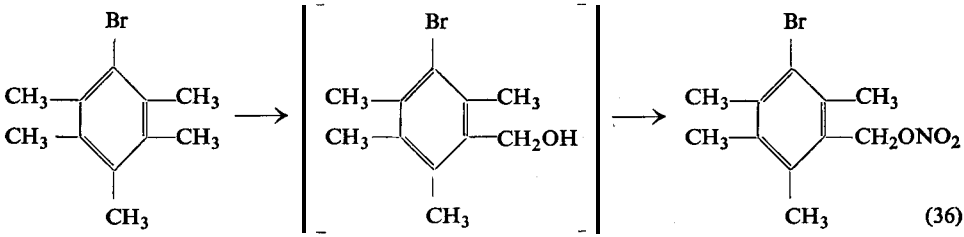
A monographic description of aromatic nitration and modern approach to substitution rules was recently given by de la Mare and Ridd [78a].

SIDE REACTIONS IN THE NITRATION PROCESS

A nitration reaction is always accompanied by side reactions which depend on such different factors as the nature of the substance being nitrated, the composition of the nitrating acid and the general nitration conditions.

Thus, oxidation reactions occurring along with a nitration reaction are particularly strong, whenever the aromatic ring is liable to such a reaction (e.g. oxidation of phenol to oxalic acid, oxidation of methyl groups in benzene homologues to hydroxymethyl and carboxyl group, oxidation of naphthalene to phthalic acid etc.).

According to Nightale [79] the action on polyalkylbenzene of concentrated nitric acid (d = 1.5) leads to oxidation of an alkyl group to yield an alcohol and possibly a nitrate, e.g.:

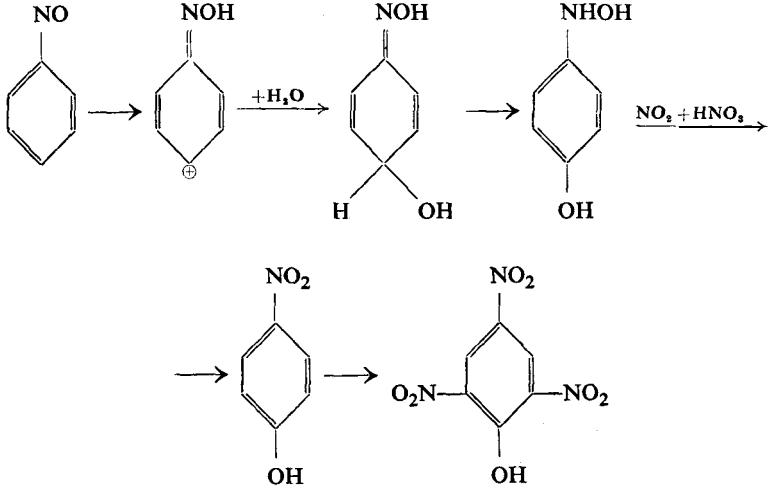


(36)

An aromatic nucleus not yet substituted with the nitro group is also readily oxidized to form phenols. That is the reason why certain quantities of nitrophenols are formed when nitrating benzene to nitrobenzene, and certain nitrocresols when

nitrating toluene. Since the phenolic group thus introduced then promotes the introduction of the nitro groups, the number of the latter may be relatively large. Thus, in the nitration of naphthalene to nitronaphthalene, 0.5-3.5% of 2,4-dinitro-α– naphthol is formed (Fierz-David and Sponagel [80]). Titov [39] found dinitrophenol and picric acid in the products resulting from the nitration of benzene, trinitro-m-cresol in the products of the nitration of toluene and trinitro-m-chlorophenol in the products of nitrating chlorobenzene.

Titov believes that phenols are formed from hydrocarbons under the influence of the nitrosyl ion, NO^+ A nitroso compound forms first, which then undergoes a rearrangement :



(37)

Another scheme of Titov [32,39] suggests that the mechanism of oxidation operates through the formation of an aryl nitrate, which is the result of attaching NO_2^+ through the oxygen atom:

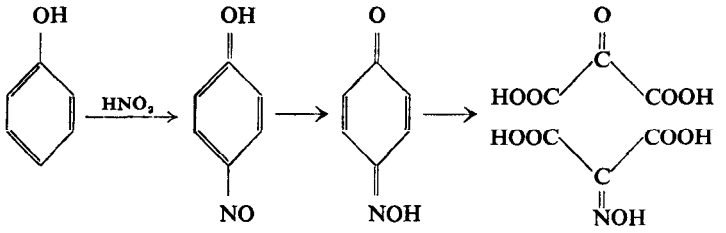
$$Ar\text{-}H + O{=}N^+{=}O \rightarrow Ar\text{-}O\text{-}N{=}O + H^+ \quad (38a)$$

$$Ar\text{-}O\text{-}N{=}O + H^+ \rightarrow Ar\text{-}OH + NO^+ \quad (38b)$$

A similar hypothesis was suggested by Bennett [35] in 1945.

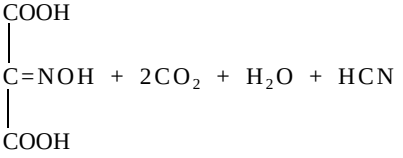
Oxidation followed by decomposition of the molecule may result in the formation of nitrated aliphatic compounds, as for example tetranitromethane and chloropicrin in the nitrations of toluene or chlorobenzene respectively.

Along with nitration processes, isomerization processes may take place which in turn may lead to various fairly complex reactions. As a result such products as CO_2, CO, NH_3 are formed. Such reactions are particularly notable in the nitration of phenols. Their mechanism has been explained by Seyevetz [81] in the following way. A phenol undergoes nitrosation under the influence of nitrous acid present in the nitrating acid. Nitrosophenol isomerizes to quinone oxime, which oxidizes at the double bonds to form mesoxalic acid and its oxime:

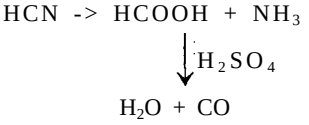


(39)

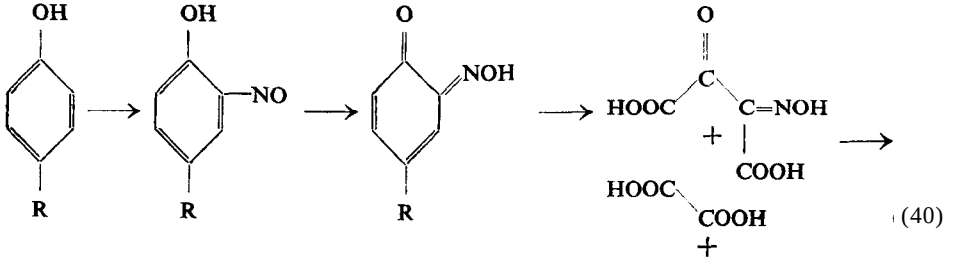
The oxime decomposes giving off hydrogen cyanide:



As is well known, hydrogen cyanide hydrolyses to form formic acid and ammonia, the formic acid being readily decomposed in concentrated acid with the evolution of CO:

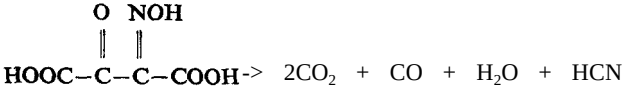


If the *para* position on the phenol nucleus is occupied, *o*- quinone oxime is formed and the reaction proceeds in a similar way, but with the formation of oxalic acid and dioxysuccinic acid oxime, which then decomposes, giving off HCN:



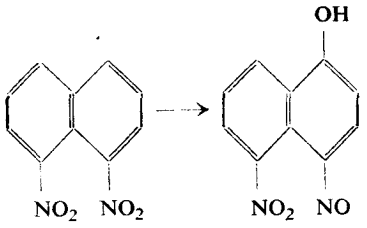
(40)

oxidation products of alkyl R



Similarly the nitration of dimethylaniline yields *p*- nitroso derivative, which undergoes similar reactions, to form HCN.

According to Seyewetz [81] not only phenols can undergo such a reaction in the nitration process. This opinion is based on Graebe's observation [82] that nitronaphthalenes isomerize to nitrosonaphthols under the influence of fuming sulphuric acid :



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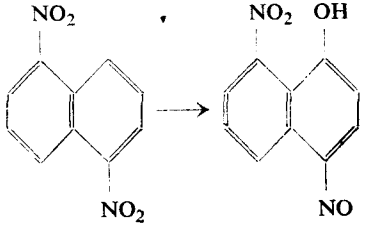
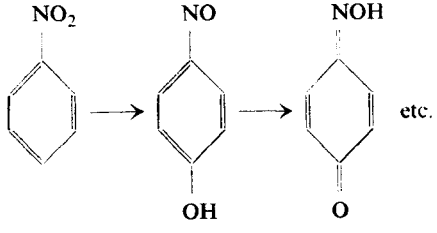


(42)

On this ground Seyewetz assumes that all nitro compounds with a free *para* or *ortho* position can isomerize in the following way:

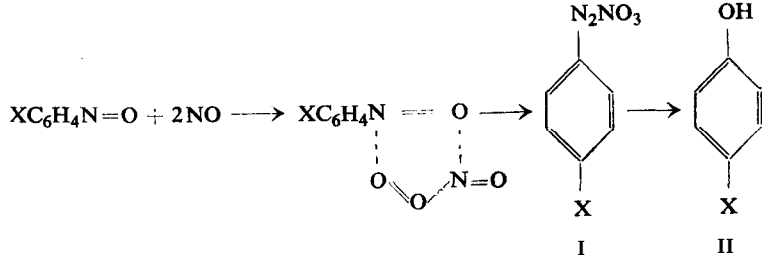


(43)

Indeed Pascal [83] found that in the waste acid from the nitration of naphthalene to dinitronaphthalene, the NH_3 content amounted to 0.001-0.002%, based on the naphthalene used for nitration.

During the nitration of aromatic compounds a certain amount of diazo compounds as by-products can also be formed. This for the first time was described by Weselsky as early as in 1875 [84] in the case of nitration of phenols with nitrogen dioxide and of nitration of aromatic hydrocarbons by Titov and Baryshnikova [85].

Titov [39] explained the reaction as the result of reaction of nitroso compounds with NO:



The diazo compound (I) can next be transformed into the phenol (II) (see also [18a]).

In some experimental conditions aromatic hydrocarbons, particularly those with alkyl side chains can form dark coloured, reddish-brown by-products on

nitration. They are often formed when the quantity of nitration acid is inadequate. An excess of nitrating mixture above the theoretical quantity prevents the formation of these products.

According to Battegay [86] benzene can give the dark coloured substances in the presence of nitrogen dioxide and sulphuric acid. He postulated the existence of a complex product of the general formula

$$(C_6H_6)_x(ONOSO_3H)_y(H_2SO_4)_z$$

Orlova and Romanova [87] established that toluene yields a dark coloured complex of the composition:

$$C_6H_5CH_3.2ONOSO_3H.3H_2SO_4$$

The following are factors which favour the formation of the complex: high temperature, and a high content of nitrogen oxide in the nitrating mixture. The complex can be destroyed by an excess of nitric acid when the concentration of nitrating mixture is high enough and nitrotoluenes result from this destruction. If the quantity of nitric acid is too low, the complex is liable to decomposition with foaming and formation of tarry matter, which is the product of both: nitration and oxidation.

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CHAPTER III

NITRATION AGENTS AND METHODS MORE RARELY USED

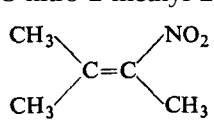
NITRATION with concentrated nitric acid or its mixture with sulphuric acid has already been described and several examples will be given in those chapters dealing with the preparation of nitro compounds. Methods more rarely used which have already been applied in practice or may be in future, are described in this chapter.

They are concerned both with using less common nitrating agents and with nitrating substances which do not yield products of great practical importance (at least at present). Such, for example, is the nitration of olefins or acetylenes.

NITRATION OF ALKENES AND ALKYNES WITH CONCENTRATED NlTRIC ACID

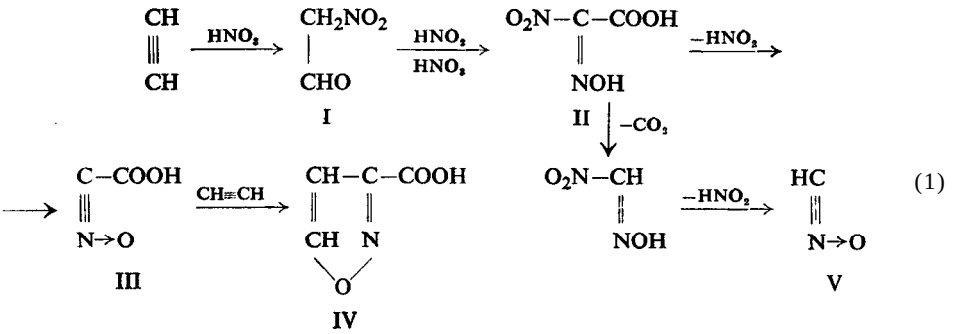
Some instances of the nitration of olefins havea heady been described in dealing with the problem of adding a molecule of nitric acid to a double bond. Besides adding concentrated HNO_3 to olefins, true nitration of olefins through electrophilic substitution can take place to yield nitroolefins. As early as in 1839 E. Simon [1], on cautious nitration of styrenes, obtained "nitrostyrene", which, according to Alekseyev [2], proved to be *o*- nitrostyrene. Lipp [3] in 1913 also found that the action of nitrous acid on camphene resulted in the formation of ω– nitrocamphene, along with addition products. In 1878 Haitinger [4] found that the nitration of isobutylene with anhydrous nitric acid led to several products, among which was nitroisobutylene $(CH_3)C_2{=}CHNO_2$, in 10% yield.

In 1935, Michael and Carlson [5] reported that with fuming nitric acid trimethylethylene gave crystalline 3-nitro-2-methyl-2-butylene in 20% yield:



More recently Petrov and Bulygina [6] investigated in detail the conditions under which several olefins can be nitrated. They found that good yields could be obtained with concentrated nitric acid reacted with olefins at *ca.* 60°C, and with less concentrated at a slightly higher temperature, i.e. 80-90°C. Nitration was also possible with 20% nitric acid, containing nitric dioxide when reacted at 70°C. Probably, according to Titov's theory (p. 88, 118) nitric dioxide is the

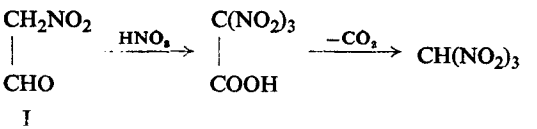
nitrating agent, while the role of nitric acid is to regenerate the NO_2 radical. The course of the reaction between acetylene and nitric acid is much more complicated. By passing acetylene through fuming nitric acid at ordinary temperature in 1901 Baschieri [7] and in 1902 Mascarelli and Testoni [8] obtained, besides nitroform, $CH(NO_2)_3$, two other crystalline compounds: an acid $C_4H_3O_3N$ and an explosive, $C_4H_2O_7H_6$ [9]. A thorough investigation of these substances was carried out by Quilico and Freri in numerous papers published between 1929 and 1932 [10,11]. They recognized that these compounds were all isoxazole derivatives (II) and they established their structure and mechanism of formation. The following is the scheme drawn up by Quilico [10] and Quilico and Simonetta [12] in 1946. It is closely related to the classic interpretation by Wieland [13,14] of the formation of fulminic acid from ethanol, nitric acid and mercuric nitrate (Vol. III):



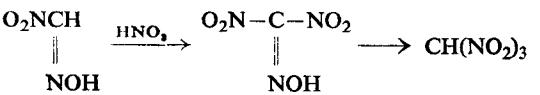
(1)

Here, isoxazole-3-carboxylic acid (IV)-the main product of the reaction-is formed from nitrile oxide (III) on adding acetylene to it.

The formation of nitroform is presented by Quilico as follows:



(2)



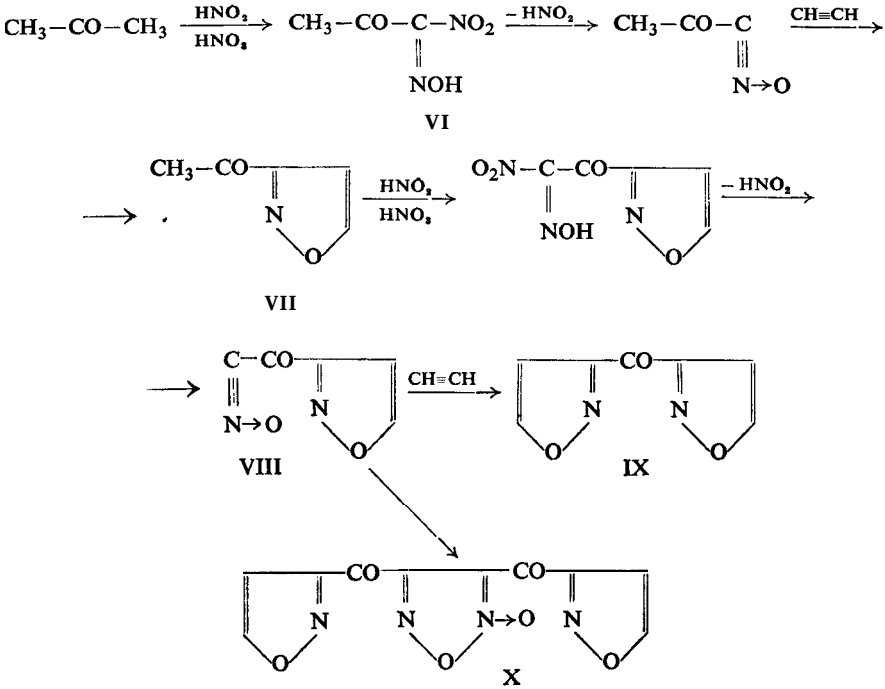
(3)

From compound III the loss of CO_2 could lead directly to the formation of fulminic acid (V) which in Wieland's scheme would take its origin from (II) through loss of CO_2 and HNO_2.

In the presence of mercuric nitrate, a high yield of tetranitromethane is obtained through the intermediate formation of nitroform. This reaction is dealt with on p. 594 (manufacture of tetranitromethane).

Experimental support for this mode of formation of the isoxazole derivative (IV) was found in 1946 by Quilico and Simonetta [12]. They obtained V from

acetylene and the ethyl ester of II reacted at room temperature in nitric acid solution. 3,3-Diisoxazolylketone (IX) is formed in a similar way from acetylene, acetone and nitric acid, according to Quilico and Freri [10] and Quilico and Simonetta [12]:



(4)

Acetyl methyl nitrolic acid (VI) is the well known product of the reaction of HNO_3 on acetone. After loosing HNO_2 it condenses with acetylene to yield 3-acetylisoxazole (VII). Through the same sequence of reactions it eventually forms IX. Dimerization of the nitrile oxide (VIII) yields diisoxazoylfuroxane (X).

All the isoxazole derivatives formed from acetylene belong to the 3-monosubstituted series (Quilico [12a]).

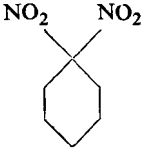
On the formation of furoxane derivatives see also Wieland's work on the action of N_2O_3 on unsaturated compounds p. 101.

NITRATION WITH DILUTE NITRIC ACID

Konovalov [15] nitrated aliphatic hydrocarbons in sealed tubes at 120-130°C, using dilute nitric acid of concentration 6.5-19%. From normal hydrocarbons he obtained secondary nitro compounds in yields varying from 40% (2-nitrohexane from hexane) to 49-50% (2-nitrooctane from octane). Aromatic hydrocarbons with an aliphatic substituted group when nitrated under the same conditions gave nitro derivatives with a nitro group in the side chain. For example, ethylbenzene, when nitrated with 12.5% nitric acid at 105-108°C, gives phenylnitroethane in 44% yield. The optimum yield is obtained with 13% acid.

Cycle-polymethylenic hydrocarbons can also be nitrated with dilute nitric acid (e.g. Wichterle [15a]).

Grundman and Haldenwanger [70] nitrated cyclohexane with nitric acid (34% HNO_3) at 122°C under 4 atm pressure. Nitrocyclohexane and gem-dinitrocyclohexane (I) resulted (m. p. 218ºC).



I

Aromatic hydrocarbons, e.g. benzene, are not nitrated with dilute nitric acid.

On the contrary, olefins can readily be nitrated to nitroolefins by means of 12.5% nitric acid as shown by Konovalov [15].

The tertiary carbon (>CH) is nitrated most readily, the secondary one (-CH_2) with some difficulty, and the primary one (-CH_3) with greater difficulty. Oxidation products, as for example acids, are formed along with nitro compounds.

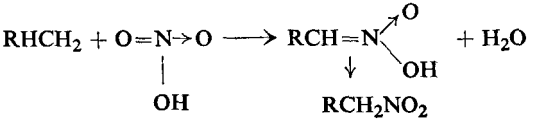
These classical studies were continued by Markovnikov [16] in 1898 and Nametkin [17] in 1908. The principal conclusions of Nametkin are:

(1) Within certain limits the nitration yield does not depend on the concentration of nitric acid, but on the quantity of the acid; for example, the same yields are obtained with 47.5% nitric acid (sp. gr. 1.3) as with 13.5% nitric acid (sp. gr. 1.075).

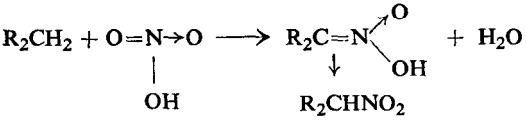
(2) The nitration rate depends on temperature, pressure and the concentration of the acid. The higher the temperature and pressure and the stronger the acid, the higher the reaction rate.

(3) The quantity of nitric acid used for nitration affects the direction of the reaction. A long run treating with an excess of nitric acid at a high temperature enhances the formation of oxidation products.

Nametkin presents the nitration mechanism as follows:



(5)



(6)

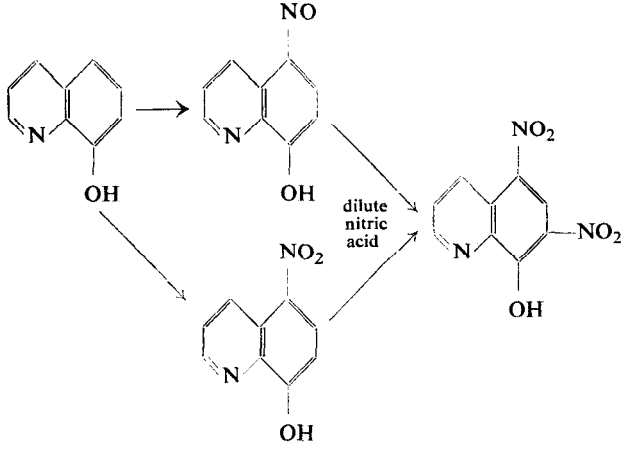
The author believes the labile forms with the -C=N bond are obtained as intermediates and subsequently they isomerize to form nitro compounds.

Phenols can be nitrated with very dilute nitric acid. Thus, Cumming, Hopper and Wheeler [18] reported that phenol can be converted into nitrophenol by

3% nitric acid, while 4% acid converts methyl- and ethyl-acetanilide into the corresponding dinitro derivatives. In 1958 T. Urbanski [19] found that 8-hydroxyquinoline can be converted to the 5,7-dinitro compound by boiling with 8% nitric acid and more recently he and Kutkiewicz [20] have found that the same result can be obtained by prolonged boiling with nitric acid of concentrations as low as 0.5%. However, the reaction occurred only after a certain induction period which ended by evolution of nitrous fumes. When $NaNO_2$ was added to the nitric acid, the reaction started almost immediately. The nitration of 8-hydroxy-5-nitrosoquinoline leads readily to formation of the same nitration product without the induction period.

The introduction of the 5-nitro group can easily be explained by nitrosation of 8-hydroxyquinoline in position 5 and subsequent oxidation of the nitroso compound. No similar explanation can be given with regard to the mechanism of the introduction of the second nitro group, in position 7, as no nitrosation of nitrophenols is known and the formation of "8-hydroxy-5-nitro-7-nitrosoquinoline", does not seem to be possible. The formation of "5,7-dimtroso-8-hydroxyquinoline" as an intermediate is also improbable because no instance of the introduction of two nitroso groups into a monophenol is known. Thus nitration most likely procedes through the formation of the 5-nitroso derivative only.

It has also been found that 5-nitro-8-hydroxyquinoline can be nitrated with 1% nitric acid to yield 5,7-dinitro-8-hydroxyquinoline. This excludes nitrosation as an intermediate step for the reason given above:



(7)

The introduction of the nitro group into position 7 would support the view already expressed (p. 48) that the NO_2^+ ion is not the only nitrating agent.

Slavinskaya [21] in 1957, found that phenol can be nitrated to *o*-, *p*- and 2,4-dinitrophenol using nitric acid dissolved in ethyl nitrate at a concentration as low as 0.5% HNO_3. Phenetole and naphthalene can also be nitrated with this solution to yield mononitro products. The presence of NO_2 was essential for successful nitration at such a low concentration of HNO_3.

ELECTROLYTIC NITRATION

Electrolytic nitration was first proposed by Triller [22] in 1897. This author pointed out that with nitric acid of concentration 52% HNO_3 at 80°C α– nitronaphthalene free from dinitronaphthalene can be obtained at the anode. With nitric acid of concentration 65% HNO_3 dinitronaphthalene is obtained. Fichter and Plüss [23] checked the Triller's patent in 1931 by carrying out simultaneous experiments with ordinary and electrolytic nitration. They found that the electrolytic method did indeed provide higher yields of α– nitronaphthalene. But the authors believed this was due not to a higher concentration of nitric acid (or more exactly of NO_3^- ions) at the anode, but rather to a rise of temperature over this area. Contrary to this view, Calhane and Wilson [24] came to the conclusion that it was the formation of a layer of high concentration around the anode that accounted for the increase in the yield.

Kirk and Brandt [25] nitrated toluene with a mixture of nitric and sulphuric acids both by the usual method and by the simultaneous use of the electrolytic method and found that with the latter technique higher yields could be obtained. Atanasiu and Belcot [26,27] treated aromatic hydrocarbons with a much dilute nitric acid (at a concentration insufficient for nitration) and, due to the electrolysis, which they carried out simultaneously, they succeeded in obtaining nitration in the anode area. In studying the reaction they observed particularly vigorous oxidation processes.

Edwards [28] carried out experiments in 1950 comparing the nitration of toluene under ordinary conditions with that combined with simultaneous electrolysis and found that higher yields of nitro compounds resulted when electrolysis was applied.

NITRATION WITH NITRIC ACID VAPOUR

The nitration of aliphatic hydrocarbons may be accomplished in the vapour phase, at 410-430°C, using nitric acid vapour. A number of papers describing this method of nitration were published by Hass and co-workers [29] between 1936 and 1940.

Under the influence of a high temperature during the reaction the hydrocarbon chain is split off to give shorter ones and such compounds as nitromethane and nitroethane are formed. For example, the authors obtained the following products in the nitration of n-pentane at 400°C:

nitromethane	1.1%
nitroethane	7.2%
1-nitropropane	13.8%
1-nitrobutane	12.5%
1-nitropentane	20.6%
2-nitropentane	20.8%
3-nitropentane	23.0%

Higher temperature enhances the formation of nitroparaffins with shorter chains.

This is seen clearly in Table 10, which shows the results of nitration of butane at various temperatures.

TABLE 10

COMPOSITION OF THE PRODUCTS OF THE BUTANE NITRATION AT VARIOUS TEMPERATURES

Temperature °C	Nitromethane %	Nitroethane %	1-Nitropropane %	2-Nitropropane %	1-Nitrobutaue %
395	2.1	12.7	4.9	4.9	30.5
393	6.0	19.0	7.0	41.0	27.0
445	5.9	18.2	6.5	37.0	31.8
450	9.0	25.0	7.0	28.0	31.0

Apart from this, at higher temperatures the amount of primary nitropropane increases as compared with the secondary derivative.

Similar experiments have been carried out by Grundmann [30]. He found 160-180°C to be the best temperature for the reaction. The products of nitration of long-chain paraffins were mono- and polynitro compounds.

Thus n-dodecane was nitrated at 180-190°C to yield the products shown in Table 11.

TABLE 11

NITRATION OF n-DODECANE

Mol. ratio n-dodecane:HNO_3	Products			
	Unreacted n-dodecane	Mononitro dodecane	Polynitro dodecane	Fatty acids
2:1	58	36	5	1
1:1	43	40	15	2
1:2	33	25	38	4
1:4	24	4	47	25

Hass and Alexander [31] and G. B. Bachman, Hass and Addison [32] described the positive influence of oxygen on the yield in gas-phase nitration. Bachman and his co-workers also discovered that the addition of halogens had a positive effect on the yield of the nitration.

Hass and Shechter [33] have formulated thirteen general rules governing the vapour-phase nitration of paraffins (and cycloparaffins). Here they are in a summarized form :

(1) Polynitro compounds can probably be formed only from paraffins of fairly high molecular weight.

(2) Any hydrogen atom in the hydrocarbon is capable of replacement by a nitro group, and the ease of replacement is: tertiary > secondary > primary group. As the temperature rises, however, the ease of replacement tends to become equal.

(3) Any alkyl group present in the paraffin can be replaced by a nitro group, i.e. chain fission takes place. Thus, isopentane yields nine nitroparaffins. The fission reaction increases as the temperature rises.

(4) Oxidation always accompanies nitration, resulting in the formation of nitro compounds and a mixture of acids, aldehydes, ketones, alcohols, nitrites, nitroso compounds, nitroolefins, polymers, carbon monoxide and carbon dioxide. Catalysts such as copper, iron, platinum oxide, etc., accelerate oxidation rather than nitration.

When considering the mechanism of nitration of paraffin hydrocarbons with nitric acid Titov [34] assumed in his papers dating from 1937 to 1948 that nitrogen oxides, NO_2 and NO, were the nitrating agents for aliphatic chains. The role of nitric acid would consist in regeneration of nitrogen oxide by oxidation of the lower nitrogen oxides formed during the reaction. Moreover, Titov assumed the nitration reaction to be a free radical one. In the first stage, a hydrocarbon is converted into a free radical under the influence of a nitrating agent:

$$RH + NO_2 \rightarrow R. + HNO_2 \qquad (8)$$

Subsequently, a free radical reacts with nitrogen oxides, also in the form of free radicals to form a nitro compound, nitroso compound or nitrite:

$$R. + .N{=}O \rightarrow RNO$$

Nitroso compound

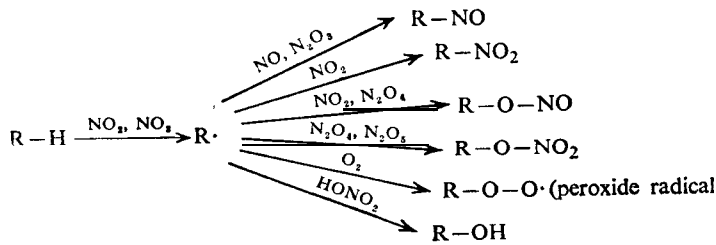
$$R. + .NO_2 \rightarrow RNO_2$$

Nitro compound

$$R.+ .ONO \rightarrow RONO \qquad (9)$$

Nitrite

Since Titov believed that the NO_3 radical might also be present in the vapour phase, he gave the following overall scheme for the reaction of NO_2 and NO_3 with a hydrocarbon RH, and for the reactions of NO, NO_2, N_2O_4, N_2O_3, N_2O_5, HNO_3 and O_2 with a free radical R:



It can be seen that nitrites and nitrates, peroxides and alcohols are formed along with nitroso and nitro compounds. The nitroso compounds (secondary)

isomerize to give oximes. The nitrites give lower aldehydes, ketones and lower radicals which form lower nitro compounds. The alcohols oxidize to aldehydes and ketones, and the latter to acids, which may yield esters with alcohols. The nitrates may give off a HNO_3 molecule to form olefins, and the latter may give dinitro compounds, etc. The nitroso compound formed may subsequently give a dinitro derivative (Ponzio [35]); for example:

$$C_6H_5CH_2NO \rightarrow C_6H_5CH{=}NOH \xrightarrow{N_2O_4} C_6H_5OH(NO_2)_2 \qquad (10)$$

Titov's experiments have shown that the nitration of alkyl-aromatics may lead not only to formation of ω– nitro compounds, but of ω– dinitro compounds as well.

McCleary and Degering [36] present a different mechanism for the nitration of paraffins with the nitric acid vapour, although like Titov they also assume the formation of free radicals:

$$\begin{gathered} RH + (\text{oxidizing agent}) \rightarrow R. + .H \\ R. + HONO_2 \rightarrow RNO_2 + .OH \\ RH + .OH \rightarrow R. + H_2O \text{ etc.} \end{gathered} \qquad (11)$$

Yet another mechanism (11) with free radicals taking part has been suggested by Boord [37]:

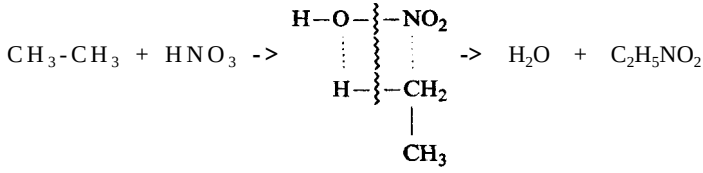
$$\begin{gathered} HONO_2 \rightarrow HO. + .NO_2 \\ RH + HO. \rightarrow R. + H_2O \\ R. + -NO_2 \rightarrow RNO_2 \end{gathered} \qquad (12)$$

By analogy with the chlorination mechanism, in which we assume a chain reaction, Boord also suggests another chain mechanism with repeating links. He assumes that nitric acid undergoes decomposition at a high temperature to form nitric anhydride :

$$\begin{gathered} 2HONO_2 \rightarrow NO_2\text{-}O\text{-}NO_2 + H_2O \\ NO_2\text{-}O\text{-}NO_2 \rightarrow .NO_2 + .ONO_2 \\ RH + .ONO_2 \rightarrow R. + HONO_2 \\ R. + NO_2\text{-}O\text{-}NO_2 \rightarrow RNO2 + .ONO2 \end{gathered} \qquad (13)$$

However, Hass and Riley [38] assume that the nitration of aliphatic hydrocarbons proceeds through the formation of addition products which subsequently undergo a breakdown which may (in the case where a certain kind of the addition product is formed) involve the rupture of C-C bonds:

$$CH_3 - CH_3 + HNO_3 \rightarrow \begin{array}{l} HO\text{–}\{\text{–}NO_2 \\ \vdots\ \{\ \vdots \\ H_3C\text{–}\{\text{–}CH_3 \end{array} \rightarrow CH_3OH + CH_3NO_2 \qquad (14)$$



(15)

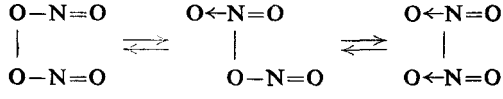
The nitration theory, which assumes that a free radical takes part, seems to be more probable than the addition theory and is in better agreement with the experimental data. An interesting piece of evidence for the participation of free radicals in the reaction was given by McCleary and Degering [36], who obtained a mixture of nitroethane and ethyl nitrate when nitrating tetraethyl lead with nitric acid in an atmosphere of CO_2, at 150°C. It is probable that the reaction proceeds as follows:

$$(C_2H_5)_4Pb \rightarrow Pb + 4C_2H_5.$$
$$C_2H_5. + HONO_2 \rightarrow C_2H_5NO_2 + OH.$$
$$C_2H_5. + OH. \rightarrow C_2H_5OH \qquad (16)$$
$$C_2H_5OH + HONO_2 \rightarrow C_2H_5ONO_2 + H_2O$$

NITROGEN DIOXIDE

As is well known, nitrogen dioxide exists as the dimer N_2O_4, at low temperatures, and as the monomer, NO_2, at high temperatures. Its boiling point is 21°C, and its density at 0°C d = 1.49 g/cm^3.

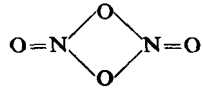
On the basis of the observation that the addition of nitrogen dioxide to compounds with double bonds yields not only nitro compounds, but nitrous acid esters as well (p. 99). Schaarschmidt [38a,39,40] expressed the view that nitrogen dioxide exists in three forms which are in equilibrium. This may be represented in modern symbols in the following way:



(a) (b) (c)

the equilibrium being shifted towards the (c) form.

More recent thermochemical studies (Giauque and Kemp [41]), and spectral work (Millen [42]), as well as determination of the dielectric constant (Addison and Lewis [43]), indicate that formula (b) seems to be the most probable. Formula (d) is possible, but less probable.



(d)

The stereo-structure, including bond distances and bond angles of vapour phase NO_2 (Fig. 17), was investigated by Maxwell and Mosley [44] in 1940 by electron

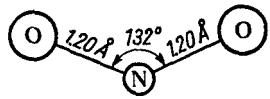


FIG. 17. Bond distances and angles of nitrogen dioxide (Maxwell and Mosley [44]).

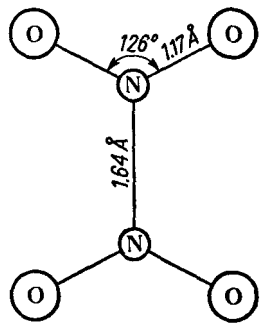


FIG. 18. Bond distances and angles of dinitrogen tetroxide (Broadley and Robertson [45]).

diffraction and the stereo-structure of solid N_2O_4 (Fig. 18) was determined in 1949 by X-ray analysis by Broadley and J. M. Robertson [45].

The ability of N_2O_4 to react in various ways suggested that the substance can also undergo heterogeneous dissociation in various ways. Three modes of ionization of N_2O_4 in dilute solutions are known. In water NO_2^- and NO_3^- are produced, in strong acids, such as sulphuric acid, NO^+ and NO_2^+ are formed, and under other conditions intermediate ionization leads to formation of NO^+ and NO_3^-. Clusius and Vecchi [46] found, when dissolving tetramethylammonium nitrate $(CH_3)_4N^+ {}^{15}NO_3^-$ labelled with ^{15}N isotope in N_2O_4, that complete exchange of the ^{15}N isotope took place according to the equation:

$$N_2O_4 \;<\!\!-\!\!>\; NO^+ + NO_3^- \qquad (17)$$

N_2O_4 in nitric acid solutions dissociated in the same way, as Goulden and Millen [47] found, when examining Raman spectra of such solutions.

Millen and Watson [48] confirmed this observation by examining the infra-red spectra of the same solutions. Very recently Goulden, Lee and Millen [48a] examined the electrical conductances of solutions of dinitrogen tetroxide in nitric acid and came to the conclusion that N_2O_4 is subjected to nearly complete ionization according to eqn. (17).

There is no evidence that the heterolytic dissociation may have the form (18) which was accepted in earlier days:

$$N_2O_4 \;<\!\!-\!\!>\; NO_2^+ + NO_2^- \qquad (18)$$

However, a homolytic dissociation into free radicals NO_2 is possible:

$$N_2O_4 \quad <-> \quad 2NO_2 \tag{19}$$

This has been confirmed by experiments on the addition of N_2O_4 to asymmetrically substituted olefins (Shechter and Conrad [49]). The most recent review of the chemistry of nitrogen dioxide is that of Gray and Yoffe [50] published in 1955.

The experiments of Falecki, Mint, Slebodzinski and T. Urbanski [185a] mentioned below also suggest that under the action of γ– radiation dinitrogen tetroxide is split mainly into ions NO_2^+ or (even more likely) into free radicals $.NO_2$ (according to eqn. 19).

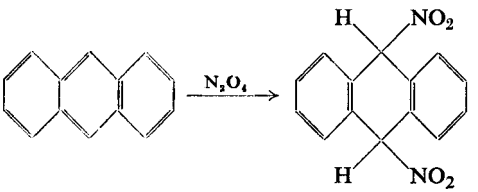
NITRATION WITH NITROGEN DIOXIDE ALONE

Aromatic compounds

The nitration of aromatic compounds with nitrogen dioxide was mentioned by Hasenbach [51] as early as 1871. He observed that when treating benzene with N_2O_4 (N_2O_4 <-> $2NO_2$) at room temperature for 7 days, nitrobenzene was formed along with oxalic acid. Leeds [52] also found picric acid in the reaction products. On treating toluene with N_2O_4 he obtained nitro derivatives of phenols and benzoic acid apart from nitrotoluenes. Naphthalene was nitrated similarly to give nitro and hydroxynitro derivatives.

When nitrating anthracene with N_2O_4 at a temperature of 10-15°C Liebermann and Lindermann [53] obtained nitro derivatives of this hydrocarbon.

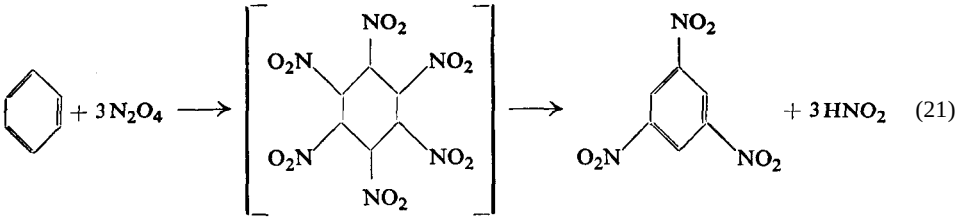
Meisenheimer's observation [54], in 1904, that anthracene combined with nitrogen dioxide to form meso-dihydrodinitroanthracene, was of special importance :



(20)

It inspired Wieland [55] in 1921 to investigate the possibility of nitrating aromatic compounds with nitrogen dioxide.

When studying the action of nitrogen dioxide on benzene at 80°C Wieland found 1,3,5-trinitrobenzene and picric acid were present along with oxidation products (oxalic acid, CO_2). Nitrobenzene was not obtained in the reaction and a large quantity of benzene remained unconverted. Wieland tried to explain this by assuming that in the first stage of the reaction six molecules of NO_2 combine with benzene just as chlorine or bromine do under the influence of light. The hexanitrocyclohexane thus formed gives off three HNO_2 molecules to form 1,3,5-trinitrobenzene :



(21)

As a result of nitrating phenol by means of N_2O_4 at a low temperature, a mixture of *o*- and *p*- nitrophenol was obtained.

The ability of nitrogen dioxide to form addition products with aromatic compounds has been proved with polycycloketones. Thus, Lukin and Dashevskaya [56] found that benzanthrone formed an addition product with two NO_2 molecules. There is no doubt that the presence of carbonyl groups affects the ability to form addition products just as it does in the addition of nitric acid (pp. 54-55).

It has been found recently that nitrogen dioxide forms addition products with compounds having an ether bond in the molecule (i.e. oxygen, which readily yields oxonium compounds) and for example, with ethyl ether, $N_2O_4.2(C_2H_5)_2O$ (m. p. -74.8°C), and with dioxane, tetrahydrofuran and tetrahydropyran (Rubin, Sisler and Shechter [57]).

Battegay and Kern [58] treated methylaniline with nitrogen dioxide and obtained *p*- nitro-N-nitrosomethylaniline or, with nitrogen dioxide in excess, 2,4-dinitromethylaniline. From dimethylaniline *p*- nitroso- and *p*- nitrodimethylaniline have been obtained, and with an excess of nitrogen dioxide, 2,4-dinitrodimethylaniline. Similar results have been obtained by Schaarschmidt, Balcerkiewicz and Gante [39].

Extensive studies on the nitration of aromatic compounds with nitrogen dioxide have been carried out by Shorygin and Topchiyev [59] and later, since 1939, by Topchiyev [60]. Here are the most important results of their investigations.

(1) Benzene and naphthalene are nitrated with nitrogen dioxide at 18-20°C to yield mononitro derivatives. At 60°C polynitro compounds are obtained as well. Ultra-violet irradiation does not affect the nitration yield.

(2) Nitration of aromatic hydrocarbons with a side chain gives mononitro compounds with the nitro group attached either to the ring or to the side chain, with a predominance of the former. For example, from toluene at temperature 14-15°C, 46% of nitrotoluenes and 9% of phenylnitromethane were obtained.

The nitration yield seems to increase under the influence of ultra-violet radiation. For example, from *m*- xylene, 81% of nitro compounds were obtained without applying irradiation, and 99% when using it.

(3) Phenols are nitrated readily to di- and tri-nitro derivatives.

(4) The nitration of amines results partly in the formation of ring nitrated compounds and partly in formation of nitro derivatives of phenols. For example from aniline small quantities of *p*- nitroaniline were obtained along with 2,4-dinitrophenol as the principal product.

(5) Heterocyclic compounds are more difficult to nitrate. For example, from quinoline 11% of mononitroquinoline was obtained at 95-100°C, while at 155-160°C 10-12% of dinitroquinoline could be obtained; from pyridine 6% of nitropyridine was obtained at 115-120°C.

Aqueous solution of N_2O_4 has both a nitrating and a nitrosating action.

N-nitrosation and simultaneous C-nitration of secondary aromatic amines by aqueous solution of N_2O_4 has been studied by Stoermer [61] and Ruff and Stein [62]. Thus N-methylaniline yielded N-methyl-n-nitroso-p-nitroaniline.

Paraffin hydrocarbons

T. Urbanski and Slori [63] in a series of experiments described in preliminary notes between 1936 and 1938 found that normal paraffin hydrocarbons from ethane to n-nonane can be nitrated with nitrogen dioxide in the gaseous phase to give good yields. The authors have nitrated normal hydrocarbons using nitrogen dioxide in large excess. They found the temperature necessary for obtaining the best yield was the lower, the longer the hydrocarbon chain. At the same time they observed that the reaction yields rise with the chain length. The principal yields obtained by the above mentioned authors are shown below in Table 12.

TABLE 12

RELATION BETWEEN THE CHAIN LENGTH OF PARAFFIN HYDROCARBONS AND THE YIELD OF NITRATION PRODUCT

Hydrocarbon	Temperature (minimum), °C	Yield up to % (by weight)
Ethane	250	10
Propane	220	20
n-Butane	200	25
n-Pentane	200	30
n-Hexane	200	35
n-Heptane	200	40
n-Octane	200	40
n-Nonane	180	60

Apart from nitration products some oxidation products such as aldehydes and fatty acids were also obtained. Nitrolic acids were also present in the products.

Detailed experiments on nitration of n-hexane with nitrogen dioxide in the vapour phase were recently carried out by Slebodzinski, T. Urbanski *et al.* [64]. They nitrated n-hexane using the molar ratio

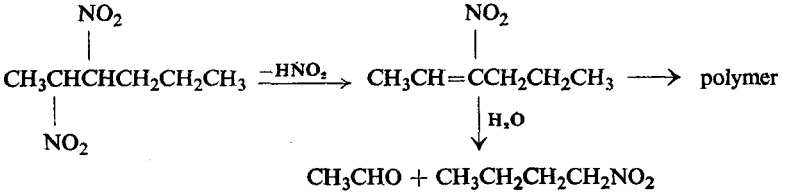
$$\frac{\text{hydrocarbon}}{NO_2} = \frac{1}{10} \text{ to } \frac{5}{1}$$

At 300°C the yield of a mixture of nitro compounds was 24-42% by weight. 27-39% of this mixture was composed of lower nitroparaffins (nitromethane,

nitroethane, l- and 2-nitropropane). Nitrohexanes (mainly 2- and 3-nitrohexanes with a small proportion of 1-nitrohexane) formed 50-60% by weight. This result would confirm the view expressed by Hass [33] and Asinger [65] on the statistical distribution of NO_2 groups in the course of nitration of long chain paraffins. A large proportion (ca. 10%) of aldehydes mainly formaldehyde and acetaldehyde and fatty acids was also found among the volatile products.

A non-volatile oily fraction which did not distil under 10 mm Hg was also formed with a yield of 10-22% by weight. This is a mixture difficult to identify, composed of various compounds of a relatively high content of nitrogen suggesting the presence of dinitroparaffins.

The authors found that dinitro compounds are readily decomposed at high temperature. This would probably proceed through nitro-olefin formation according to the scheme:

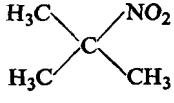


Nitrolefin- would polymerize or be hydrolysed to yield an aldehyde and lower nitroparaffin.

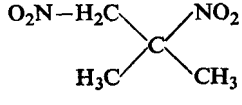
When lower reaction temperature (e.g. 220-230°) was used, the total yield of nitro compounds was lower: ca. 20%, but the proportion of primary nitrohexane was higher. Also the yield of the non-volatile fraction with a higher nitrogen content was higher (ca. 30%).

In 1949, Titov [34] obtained a larger proportion of secondary nitro compounds along with a smaller quantity of a primary nitro compound when nitrating n-pentane at 260-270°C and at a molar ratio N_2O_4:n-C_5H_{12} = 1:3.

In the nitration of a hydrocarbon having a >CH group, first of all this group was nitrated to form a tertiary nitro compound. Thus, for example, according to T. Urbanski and Wolnicki [66], isobutane gave tertiary nitroisobutane.



A quantity of the dinitro compound (primary-tertiary) was also obtained:



The same products of nitration of isobutane have been reported by Levy [66a].

According to Bachman, Hass and Addison [32] the addition of halogens (chlorine, bromine) to the reacting system hydrocarbon-nitrogen dioxide increases the yield of the nitro compounds.

Hass, Dorsky and Hodge [67] nitrated paraffins with nitrogen dioxide under pressure. They were able to nitrate methane to nitromethane.

Levy and Rose [68] reported that nitration of propane with nitrogen dioxide at 360°C under 10 atm gave a 75-80% yield of nitroparaffins. The mixture of products was composed of 20-25% nitromethane, 5-10% nitroethane, 45-55% 2-nitropropane, 20% 1-nitropropane and 1% 2,2-dinitropropane. Geiseler [69] nitrated paraffins under 4 atm at 190°C. Grundman and Haldenwanger [70] nitrated cyclohexane with nitrogen dioxide at 120-125°C under 4-5 atm and obtained both mono- and di-nitroproducts.

Titov [71] in 1948, carried out an extensive study on the nitration of aliphatic side-chain of aryl-aliphatic hydrocarbons with nitrogen dioxide. He found that, for example, the nitration of toluene may result in the formation of phenyldinitromethane along with phenylnitromethane. Low temperature facilitates the formation of the former (Table 13).

TABLE 13

RESULTS OF NITRATION OF 1000 ml OF TOLUENE WITH NITROGEN DIOXIDE AT DIFFERENT TEMPERATURES

Nitration temperature °C	Quantity of phenylnitromethane obtained g	Quantity of phenyldinitromethane obtained g
20	23.5	5.0
70	6.8	15.9
95	1.4	13.4

According to Titov the formation of phenyldinitromethane may be presented by the scheme:

$$C_6H_5CH_3 \xrightarrow{NO_2} C_6H_5CH_2. \xrightarrow{NO} C_6H_5CH_2NO \rightarrow C_6H_6CH = NOH \xrightarrow{N_2O_4} C_6H_5CH(NO_2)_2$$

Unsaturated hydrocarbons

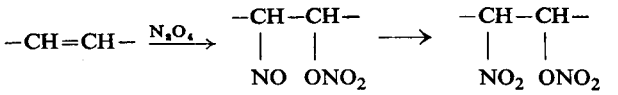
When olefin hydrocarbons react with nitrogen dioxide or nitrous and nitric anhydride they are added to a double bond. For the reactions of N_2O_5 and N_2O_3 see also pp. 106 and 109.

The addition of nitrous anhydride results in the formation of nitrosites (nitroso-nitrites) (I) :

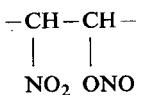
$$-CH=CH- \xrightarrow{N_2O_3} \begin{matrix} -CH-CH- \\ | \quad | \\ NO \quad ONO \end{matrix}$$

Nitrosite (I)

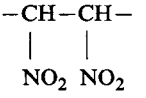
By the addition of nitrogen dioxide, nitrosates (II) (nitroso-nitrates) or dinitro compounds (III) or dinitrites (IV) are obtained. Nitrosates (II) can be oxidized to nitro-nitrates (IIa).



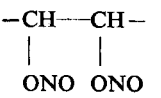
Nitrosate (II) Nitro-nitrate (IIa)



Nitro-nitrite (IIb)



Dinitro compound (III)



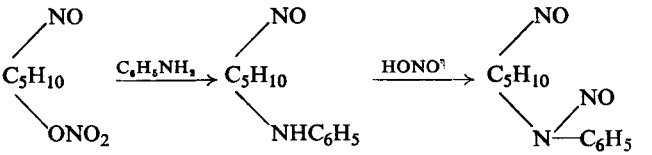
Dinitrite (IV)

Riebsomer [72] gave an extensive list of the reactions of NO_2 addition to unsaturated compounds.

Guthrie [73] obtained the first nitrosate in 1860 by treating amylene with nitrogen dioxide. Wallach [74] found it to be a well defined compound, while this is not the case with the amylene and N_2O_3 compound.

Although no amine was produced by the reduction of amylene nitrosate, and only ammonia was formed, Wallach inferred from the results of the experiments described below that the compound had the structure V.

By heating amylene nitrosate (V) with aniline in an alcoholic solution, amylene-nitrosoanilide (VI) was formed, which under the influence of nitrous acid gave the N-nitroso compound (VII):

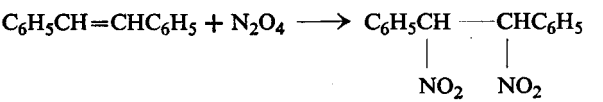


V VI VII

m. p. 140-141°C

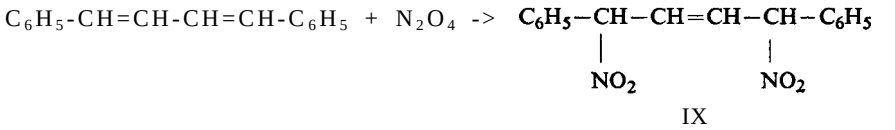
The reaction was later widely used by Wallach for the identification of terpenes, which formed well defined, crystalline nitrosates and nitrosites and also by Jagelki [75] and Lipp [3].

Extensive research work on the action of N_2O_3, N_2O_4 and N_2O_5 on olefins was carried out by Demyanov [76, 77, 78]. He found that both glycol esters and nitro compounds were obtained in these reactions. According to Wieland [13,55], the reaction of N_2O_4 with stilbene results in the formation of dinitrostilbene (VIII):



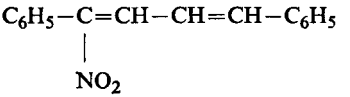
VIII

The addition of N_2O_4 to compounds with conjugated double bonds takes place in a way similar to the addition of halogens to these compounds. For example 1,4-diphenylbutadiene is converted to 1,4-diphenyl-1,4-dinitrobutylene-2 (IX) :



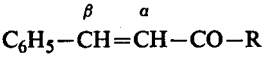
IX

A further analogy with halogen derivatives discovered by Wieland lies in the fact that compound IX, when treated with an alcoholic solution of potassium hydroxide, gives off an HNO_2 molecule to form 1,4-diphenyl-1-nitrobutadiene (X):



X

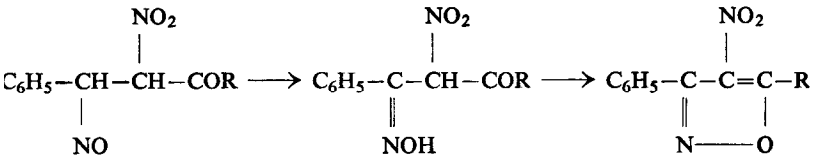
Subsequently Wieland found that on treating unsaturated compounds containing a carbonyl group, of the general formula



XI

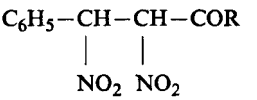
with N_2O_3 or N_2O_4, three types of compounds were obtained:

(1) On treating with N_2O_3 first the compound XII was formed which then isomerized to give the oxime (XIII), which in turn gave off water to form isoxazole (XIV):



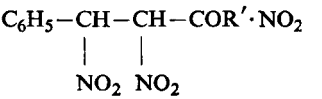
XII XIII XIV

(2) N_2O_4 was added on, giving the dinitro compound (XV):



XV

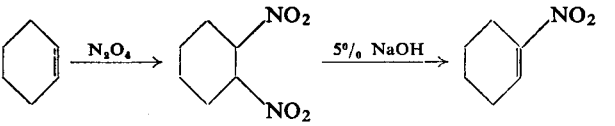
(3) The R radical attached to the carbonyl group, when treated with N_2O_4, underwent nitration:



XVI

where R'H is the radical R.

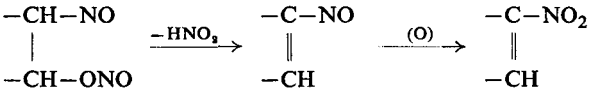
In such a way, by treating cyclohexene with N_2O_4, Wieland and Blümich [79] obtained a dinitro compound which, under the influence of an alkali hydroxide, was converted to nitrocyclohexene :



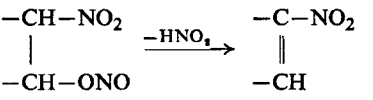
(22)

Numerous experiments on the action of nitrogen dioxides on olefins were carried out by Demyanov and Sidorenlco [76] between 1909 and 1934. They obtained products of the types IIa and III.

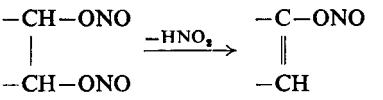
Schaarschmidt and Hoffmeier [40] found that on treating unsaturated hydrocarbon with N_2O_4 a mixture of products of the I, II, III, and IV types was obtained. Only the dinitro compounds of type III were stable. Others underwent decomposition in the following way:



I Nitrosoolefin Nitroolefin



IIb Nitroolefin



IV Unstable nitrite

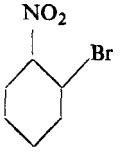
It was originally thought that the addition of dinitrogen tetroxide to the double bond of an olefin in a weakly basic solvent such as ether is a heterolytic (ionic $-NO_2^+NO_2^-$) addition.

Results of recent study, however, have been interpreted in terms of a homolytic process. Schechter and Conrad [49] have observed that the production of methyl-3-nitroacrylate and methyl-2-hydroxy-3-nitropropionate in the reaction between N_2O_4 and methyl acrylate could not be explained on the basis of heterolytic addition, but was to be expected if a homolytic process were occurring. Brown [80] has shown that olefin nitration under circumstances in which the nitronium ion (NO_2^+) is the reactant has characteristics entirely different from those of the N_2O_4-olefin reaction. Brand and I. D. R. Stevens [81] also believed the reaction of addition of nitrogen dioxide to olefins to involve radicals. According to these authors the following experimental facts provide evidence for this:

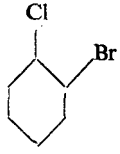
(1) Cyclohexene reacted with dinitrogen tetroxide (N_2O_4) to yield l,2-dinitrocyclohexane and 2-nitrocyclohexyl nitrite.

(2) However, in the presence of two moles of bromotrichloromethane the reaction followed a different course, and the normal products, 1,2-dinitrocyclo-

hexane and 2-nitrocyclohexyl nitrite, were not formed. Instead, the main products were : 2-bromonitrocyclohexane and 2-bromochlorocyclohexane.

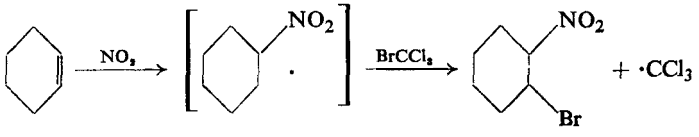


(Yield 20.6%)



(Yield 31.5%)

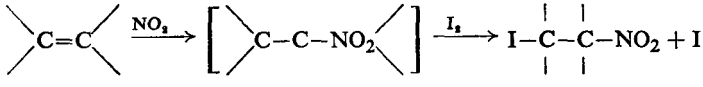
These products derive from the interaction of the intermediate β– nitroalkyl radical and the bromotrichloromethane e.g. :



(23)

The main reaction was accompanied by a number of secondary reactions.

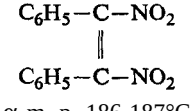
Recently T. E. Stevens and Emmons [82] examined the reaction between N_2O_4 and olefins in the presence of iodine in to order to trap the intermediate nitroalkyl radical, and they have been able to isolate β– nitroalkyl iodides in good yield:



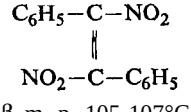
(24)

These experiments provide further proof of the radical nature of the N_2O_4-olefin addition reaction.

The nitration of acetylene hydrocarbons proceeds in a more complex way than that of olefins. The first member of the series-acetylene-undergoes various reactions, for example, with nitric acid (see p. 82 and p. 599) Tolane (diphenylacetylene) is nitrated with N_2O_4 to form dinitrostilbene. Two products are formed which are presumably α– and β– stereoisomers:

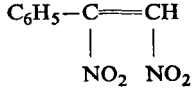


α m. p. 186-187°C

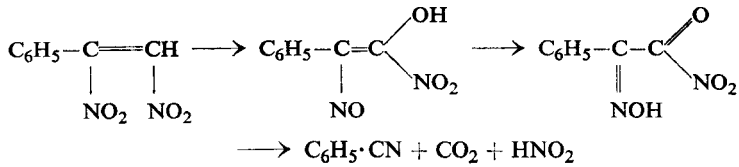


β m. p. 105-107°C

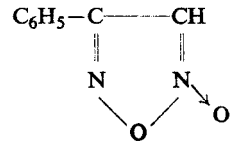
When nitrating phenylacetylene, Wieland and Blümich [79] obtained phenyldinitroethylene:



an unstable product which decomposes giving off benzonitrile, CO_2 and HNO_2, probably according to the following scheme:



Phenylacetylene reacted with N_2O_3 to yield phenylfuroxane:



(25)

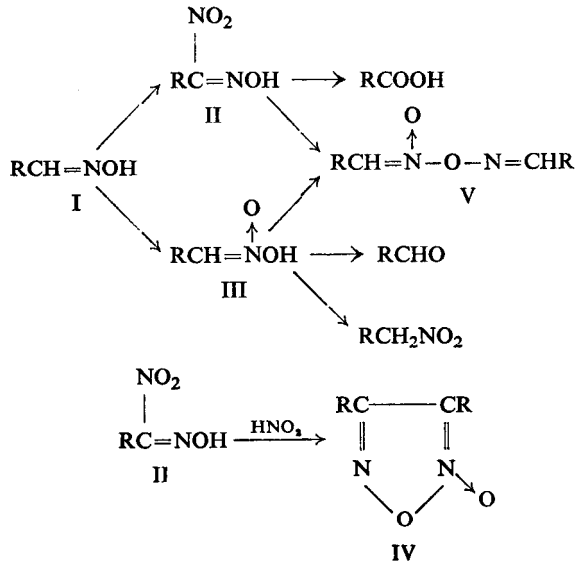
Petrov and Bulygina [6] found that under the conditions they used, transfer of the double bond into the β– position with reference to the nitro group occurred, similar to the transfer occurring in chlorination reactions, according to the mechanisms proposed by Lvov [83] and by Tishchenko [84]. For example, octene- Δ^1 gave 1-nitrooctene- Δ^2 under the action of dinitrogen tetroxide:

$$CH_2{=}CH(CH_2)_5CH_3 \xrightarrow{N_2O_4} NO_2CH_2CH = CH(CH_2)_4H_3 \qquad (26)$$

The action of dinitrogen tetroxide on aldoximes has several interesting features. This reaction has been studied by Scholl [85], Potio [35] (benzaldoxime), Mills [86] (isonitrosoacetone), and recently by Boyer and Alul [87].

The last authors investigated the reaction with acetaldoxime, propionaldoxime and benzaldoxime. They came to the conclusion that dinitrogen tetroxide both nitrates and oxidizes aldoximes. The nitration is more pronounced with increase of temperature whereas oxidation is most effective at 0°C and below.

Boyer and Alul suggest the following scheme for the reactions:



Nitrolic acids (II) are relatively stable when R is alkyl but can lose nitrous acid with furoxane (IV) formation (Wieland and Semper [14]). Aci-nitroparaffins (III) readily yield aldehydes when R is alkyl. At lower temperatures the product V ($R=C_6H_5$) predominates.

According to Ponzio [35], benzaldoxime can form phenyl-gem-dinitromethane $C_6H_5CH(NO_2)_2$, under the action of N_2O_4.

NITRATION WITH NITROGEN DIOXIDE IN THE PRESENCE OF SULPHURIC ACID

Pinck [88] studied the nitrating action of nitrogen dioxide in a sulphuric acid solution. According to this author, the nitrating action of the solution proceeds as follows, from each N_2O_4 molecule with the formation of one molecule of HNO_3 and one of nitrosylsulphuric acid:

$$N_2O_4 + H_2SO_4 \rightleftharpoons \begin{matrix} OH \\ SO_2 \\ ONO \end{matrix} + HNO_3 \qquad (27)$$

When treating 1 mole of toluene with 1.05 mole of N_2O_4 in the presence of 1.6 moles of 95 % sulphuric acid at 50-55°C for 3½ hr, the yield of nitrotoluene obtained amounted to 87.5% of theory.

According to Battegay [58], nitration with nitrogen dioxide in the presence of sulphuric acid followed a course such that an addition product of H_2SO_4 and the aromatic hydrocarbon was formed initially. Battegay assumed the sulphuric acid activated the aromatic ring in a way similar to the role of aluminium or ferric chlorides in the Friedel-Crafts reaction, or as in a chlorination reaction. Indeed, Battegay found that benzene may be readily chlorinated in the presence of sulphuric acid instead of $FeCl_3$.

Benzene activated with sulphuric acid would add on to N_2O_4 which, according to Battegay, has the structure of "nitrosyl nitrate" $NO_2.ONO$. An addition product was thought to be formed which, in the presence of an excess of sulphuric acid, would decompose to yield a nitro compound and nitrosylsulphuric acid.

$$C_6H_6 + \begin{matrix} NO_2 \\ | \\ ONO \end{matrix} + H_2SO_4 \rightarrow C_6H_5NO_2 + NSO_5H + H_2O \qquad (28)$$

Titov and his co-workers [34] proposed the following mechanism of nitration of aromatic compounds with nitrogen dioxide in the presence of sulphuric acid:

$$RH + N_2O_4 \rightarrow RNO_2 + HNO_2 \qquad (a)$$

$$N_2O_4 + H_2SO_4 \leftrightarrow HNO_3 + NSO_5H \qquad (b)$$

$$2NSO_5H + H_2O \leftrightarrow N_2O_3 + 2H_2SO_4 \qquad (c)$$

$$2HNO_3 + N_2O_3 <-> 2N_2O_4 + H_2O \quad (d)$$

$$H_2SO_4.qH_2O + H_2O = H_2SO_4.(q+1)H_2O \quad (e)$$

Thus the overall equation would be:

$$RH + N_2O_4 + nH_2SO_4.mH_2O \rightarrow RNO_2 + NSO_5H + (n\text{-}l)H_2SO_4.(m+l)H_2O$$

The principal assumption was that nitration of aromatic compounds in the medium under consideration depends on the saturation of the free valences of the sulphuric acid with nitrous acid and water. To make use of the most N_2O_4 the ratio of free sulphuric acid to the amount of water (n-1) : (m+1), should by the end of the reaction be not less than a certain minimum value, characteristic for the compound being nitrated. For benzene the value is 4:1, for chlorobenzene 5:1, for toluene 1.8:1.

When using a solution of 1.1 mole N_2O_4 in 45% oleum for the nitration of 1 mole of benzene, Titov obtained dinitrobenzene with a yield 97-89% of theory. Similarly, by treating nitrotoluene with a solution of N_2O_4 in oleum, 2,4-dinitrotoluene was obtained with a yield 98% of theory. According to Titov, 2,4-dinitrotoluene could be converted into 2,4,6-trinitrotoluene with a yield 85% of theory.

According to more recent views, nitrogen dioxide in sulphuric acid solution gives the nitrosonium ion NO^+ and a nitric acid molecule. The latter, treated with an excess of sulphuric acid, gives a nitronium ion, which is the actual nitrating agent :

$$N_2O_4 + H_2SO_4 + NO^+ + HNO_3 + HSO_4^- \quad (29)$$

$$HNO_3 + 2H_2SO_4 + NO_2^+ + 2HSO_4^- + H_3O^+ \quad (30)$$

(Ingold, Gillespie, Graham, Hughes and Peeling [89]).

NITRATION WITH NITROGEN DIOXIDE IN THE PRESENCE OF FRIEDEL-CRAFTS CATALYST

Schaarschmidt [38a] has examined the nitration of aromatic hydrocarbons with nitrogen dioxide in the presence of aluminium or ferric chloride. Benzene with N_2O_4 and $AlCl_3$ forms a red complex at about 10°C, which decomposes on adding water with the formation of a small quantity of chlorobenzene. The composition of the complex, according to Schaarschmidt, was $2AlC1_3.3C_6H_6.3N_2O_4$. When heated to 30-35°C however it underwent a transformation, followed by the formation of nitrobenzene when diluted with water:

$$2AlCl_3.3C_6H_6.3.N_2O_4 + H_2O \rightarrow 2AlC1_3.H_2O + 3C_6H_6.N_2O_4 \quad (31)$$

$$C_6H_6.N_2O_4 + H_2O \rightarrow C_6H_5.NO_2 + HNO_2 \quad (31a)$$

Titov [34] assumed a different mechanism for this reaction, suggesting that heating a hydrocarbon with nitrogen dioxide and $AlCl_3$ led to the reaction:

$$3RH + 3N_2O_4 + 2AlC1_3 \rightarrow 3RNO_2 + 3NOCl + Al_2Cl_3(OH)_3 \quad (32)$$

The nitro compound, nitrosyl chloride, and basic aluminium chloride formed a number of addition products, which are in equilibrium:

$$RH + N_2O_4 + 2AlC1_3 \leftrightarrow RNO_2.AlCl_3 + AlCl_2OH.NOCl \leftrightarrow \leftrightarrow RNO_2.AlCl_2OH + AlC1_3.NOCl \quad (33a)$$

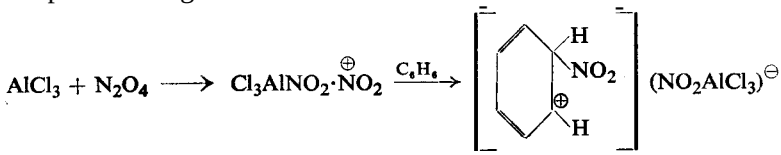
and then

$$RNO_2.AlCl_3 + N_2O_4 + RH \rightarrow AlCl_2(OH).(2RNO_2)(NOCl) \quad (33b)$$

$$AlC1_2OH.NOCl + N_2O_4 + RH + AlCl(OH)_2(RNO_2)(2NOCl) \quad (33c)$$

When heated, the complexes dissociated into their components.

Titov explained the activating action of aluminium chloride by the fact that aluminium chloride is coordinatively unsaturated and strongly polarizes the molecule of the compound being nitrated:

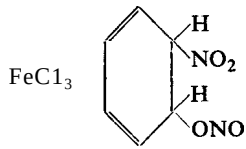


(34)

The hydrogen atom attached to the carbon atom linked to the nitro group is readily split off to form nitrobenzene.

Titov used the following technique for the nitration. A mixture of hydrocarbon and aluminium chloride was saturated with nitrogen dioxide. An exothermic reaction took place, $AlCl_3$ being dissolved. The intensity of the reaction diminished after all the aluminium chloride had been dissolved. The saturation of the mixture with NO_2 was stopped at 95% of the theoretical amount. Then the unreacted nitrogen dioxide was expelled by passing CO_2. The liquid nitro compound phase was separated from the solid aluminium salt. The yield of the nitro derivatives of toluene and chlorobenzene was 88% and 96% of theoretical for toluene and chlorobenzene respectively.

Bogdanov [90] investigated the nitration of aromatic compounds with nitrogen dioxide in the presence of ferric chloride. He assumed that in the first stage of the reaction a complex was formed:



Chlorine introduced into the mixture activated the nitration reaction by promoting the decomposition of the complex into nitrobenzene and ferric chloride, the latter again taking part in the reaction.

Among more recent work Topchiev's experiments [60] should be mentioned, in which boron fluoride was used as a catalyst for the nitration with nitrogen dioxide. At a temperature of 55-50°C and with an N_2O_4 to benzene molar ratio 0.5:1 he obtained 18% of the theoretical yield.

G. B. Bachman and his co-workers [91] investigated the action of the boron trifluoride and nitrogen dioxide complex, formed by combining the two compounds at 0°C:

$$BF_3 + N_2O_4 \rightarrow [F_3B{<}\text{-}NO_2]\text{-}NO_2^+ \quad (35)$$

Crystalline complex salt

The complex salt acted on benzene to give nitrobenzene (40% yield) and a small quantity (1.5%) of *m*- dinitrobenzene at 0°C. At room temperature only *m*- dinitrobenzene in 7% yield was formed.

The action of this reagent on naphthalene is of interest. A mixture of dinitronaphthalene isomers is formed in 65% yield, the ratio of the 1,5- to l,8-isomer being 2:1, the reverse of the ratio obtained by nitration with the ordinary nitrating mixture.

NITRATION WITH NITROGEN DIOXIDE IN THE PRESENCE OF ACTIVATED SILICA

McKee and Wilhelm [92] found that the highest yield of nitration of benzene with nitrogen dioxide in the vapour phase was obtained at 310°C. In the presence of activated silica the yield was higher than that obtained without a catalyst and could amount to 83.6%. Nitrophenol was also formed in a yield rising with temperature, so that at 330°C it was the principal reaction product. The authors supposed that the catalytic action of activated silica was probably a specific one and did not consist only in binding the water formed during the nitration process.

PHOTONITRATION WITH NITROGEN DIOXIDE

Gorislavets [93] claimed that the nitration of benzene or nitrobenzene with nitrogen dioxide readily occurred on irradiation with rays of certain definite wavelengths, which activate nitrogen dioxide.

Thus, benzene was nitrated quantitatively at the wavelengths 4000 - 7000 Å at a temperature of 55-60°C. The highest yield of dinitrobenzene was obtained at wavelengths 1800 - 2900 Å. The experiments of other workers did not confirm his results (Hastings and Matsen [94]).

On the other hand Lippert and Vogel [95] assert that on irradiation with high intensity ultra-violet light nitro compounds undergo dissociation into free radicals:

$$ArNO_2 \rightarrow Ar + .NO_2 \quad (36)$$

On the basis of this statement it may be concluded that differences in the results of various authors may be due to the difference in intensity of applied irradiation.

NITROGEN PENTOXIDE (NITRIC ANHYDRIDE)

As is well known, nitrogen pentoxide is a solid, crystalline, colourless product, melting at 30°C. Nitrogen pentoxide was first used as a nitrating agent for the O-nitration of cellulose (Hoitsema [96]; Berl and Klaye [97], and others (see Vol. II)).

Titov [34] suggested in 1941 that nitrogen pentoxide undergoes a heterolytic dissociation:

$$N_2O_5 \rightarrow NO_2^+ + NO_3^- \quad (37)$$

It is the presence of the nitronium ion that accounts for the nitrating properties of nitrogen pentoxide.

Ogg [98] studied the heat of dissolution of nitric anhydride is water, and on the basis of the results obtained came to the conclusion that the compound underwent the following reactions (a), (b), (c) and (d):

$$N_2O_5 \rightarrow NO_3 + NO_2 \quad (a)$$

$$NO_3 + NO_2 + N_2O_5 \quad (b)$$

$$NO_3 + NO_2 \rightarrow NO_2 + O_2 + NO \quad (c)$$

$$NO + N_2O_5 \rightarrow 3NO_2 \quad (d)$$

The (a) reaction corresponds to the reaction (37). Reaction (c) proceeds slowly as compared with reaction (b), while, on the contrary, reaction (d) is a fast one.

In general, the reaction of decomposition of N_2O_5, which is seemingly of the first order (according to Smith and Daniels [99], Johnston and his co-workers [100-102]), is in fact the resultant of reactions (a) and (b) and of the second order reactions (c) and (d). Indeed, Johnston [100] found the decomposition of nitrogen pentoxide in the presence of nitrogen dioxide to be a second order reaction.

In 1951, Titov and Shchitov [103] when examining the action of nitric anhydride on normal paraffins and cycloparaffins, found that in the presence of an inert solvent the reaction already started at 0°C, with the evolution of heat. Nitric acid esters were formed in the reaction which, according to the authors, proceeded through the following stages:

$$N_2O_5 \leftrightarrow .ONO_2 + .NO_2$$
$$RH + .ONO_2 \rightarrow R. + HONO_2 \quad (38)$$
$$R. + .ONO_2 \rightarrow RONO_2$$

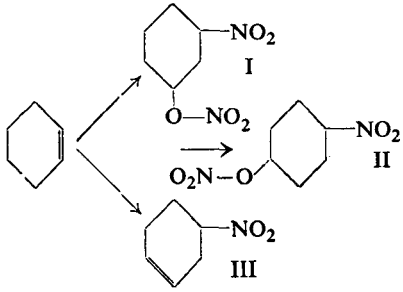
For example, from n-hexane, secondary n-hexyl alcohol nitrate was obtained:

$$\underset{\text{n-Hexane}}{C_6H_{14}} \xrightarrow{+NO_2} \underset{\text{2-Hexyl}}{C_6H_{13}\cdot} \xrightarrow[-NO_2]{+N_2O_5} \underset{\text{2-Hexyl nitrate}}{C_6H_{13}ONO_2} \quad (39)$$

NO_2 formed in reaction (39) also reacted in accordance with (8) to give a nitro compound along with an ester.

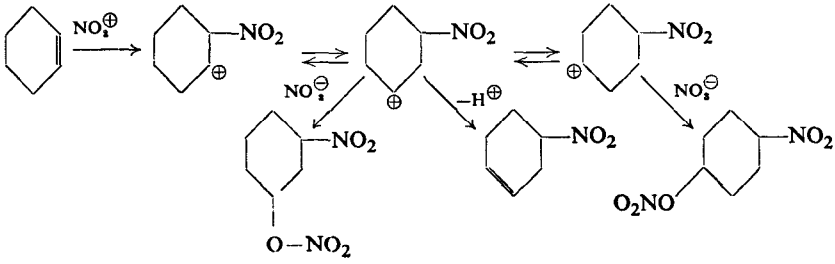
In reactions of N_2O_5 with the olefins the products obtained had structures that confirmed Titov's view on the heterolytic decomposition of N_2O_5 into NO_2^+ and NO_3^-. For example, when treating cyclohexene with nitrogen pentoxide, T. E.

Stevens and Emmons [82] obtained three compounds: the nitro-nitrates (I) and (II) as well as a nitro-olefin (III)



(40)

They suggested the following reaction mechanism:



(41)

G. B. Bachman and Hokama [104] have recently found that nitrogen pentoxide forms a complex with boron trifiuoride: $BF_3.N_2O_5$. The complex is a colourless, stable liquid in the presence of polychlorinated paraffins and a white solid in nitroparaffins. It decomposes at ca. 75°C with evolution of brown fumes.

G. B. Bachman and Dever [105] suggest that the complex has the structure

$$(F_3B{<}\text{-}ONO_2)^{-}NO_2^{+}$$

The complex seems to be a somewhat more powerful nitrating agent than an anhydrous mixture of HNO_3-H_2SO_4.

Nitrobenzene reacts with two moles of the complex in carbon tetrachloride to give an 86% yield of *m*- dinitrobenzene after 18 hr at 75°C.

Benzoic acid reacts with three moles of the complex in 36 hr at 70°C to form 3,5-dinitrobenzoic acid (70% yield) and *m*- nitrobenzoic acid (9.3% yield).

The complex forms an addition molecular compound with *m*- dinitrobenzene (m.p. 89.5°C).

NITRYL CHLORIDE (NITRONIUM CHLORIDE, NO_2Cl)

It was found by Steinkopf and Kühnel [106] that the so-called nitryl chloride is an agent that both nitrates and chlorinates aromatic hydrocarbons. However, the reaction could be selective. Thus, only *o*- nitrophenol was formed when nitryl chloride interacted with phenol below room temperature, but at room temperature 2,4-dichloro-6-nitrophenol was obtained. Naphthalene was chlorinated and nitrated simultaneously to give α– nitro- and α– chloro-naphthalene.

A very interesting result was obtained with benzene. At room temperature nitryl chloride dissolved in benzene without reacting. When warmed the nitryl chloride evaporated off unchanged. When benzene and nitryl chloride were heated under pressure, 1-chloro-2-nitrocyclohexadiene was formed and decomposed, producing nitrobenzene.

On the other hand Price and Sears [107] studied the reactions of nitryl chloride with various aromatic compounds in the presence of aluminium chloride, and found that phenol, anisole and naphthalene tended to undergo oxidative degradation. In the case of naphthalene they obtained a 31% yield of α– nitronaphthalene, whereas with anisole and phenol they were able to isolate only traces of nitro compounds without any evidence of chlorination.

Goddard and co-workers [108-111] found that nitryl chloride in various solvents at room temperature and below (-10°C) chlorinates, rather than nitrates, toluene, ***m***- and *p*- xylene, and mesitylene, though not benzene.

Thus, *p*- xylene yielded 2,5-dichloro-p-xylene. The principal reaction with anisole was also chlorination and with phenol nitration when nitration temperature was low (-80°C) both *o*- and *p*- nitrophenols were formed. At room temperature chlorination also occurred yielding 2,4-dichloro-6-nitrophenol and 3,6-dichloro-2-nitrophenol.

Steinkopf and Kühnel [106] also examined the action of nitryl chloride on ethylene and reported that only 1,2-dichloroethane was formed. Petri [112] however reported the formation of 1-chloro-2-nitroethane (with 45% yield) and 2-chloroethyl nitrate (35% yield). Ville and DuPont [113] confirmed the formation of 1-chloro-2-nitroethane (50% yield) and Goddard [111] confirmed the results of Petri. Price and Sears [107] obtained 2-chloro-1-nitropropane from propane.

Thus it should be accepted that the main reaction of ethylene (and probably olefins in general) with NO_2Cl is:

$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} \longrightarrow \begin{array}{l} CH_2Cl \\ | \\ CH_2NO_2 \end{array} + \begin{array}{l} CH_2Cl \\ | \\ CH_2ONO \end{array} \qquad (42)$$

According to Goddard, styrene reacted with nitryl chloride to yield 1,2-dichloro-1-phenylethane in 70-80% yield. Another product 1-chloro-2-nitro-l-phenylethane was thought to be present, but could not be isolated. On distillation it decomposed, evolving HCl, and *o*- nitrostyrene was obtained.

Finally T. Urbanski and Siemaszko [114] used nitryl chloride in the gas phase to O-nitrate cellulose. They obtained a stable product containing 12.2% N.

On the basis of the formation of chloroalkyl nitrites (e.g. 2-chloroethyl nitrite from ethylene) Goddard drew the conclusion that nitryl chloride could be subjected to heterolysis :

$$ClNO_2 \rightarrow Cl^+ + NO_2^- \qquad (43)$$

This dissociation would also be confirmed by the chlorinating action of the substance.

NITRYL FLUORIDE (NITRONIUM FLOURIDE, NO_2F)

Nitryl fluoride is a gas which liquifies at -73°C and solidifies at ca. -160°C.

Nitryl fluoride was prepared for the first time, by Ruff, Manzel and Neumann [115] in 1932, by acting with fluorine on nitrogen dioxide. (The earlier report of Moissan and Lebeau [116] in 1905 is uncertain.) Aynsley, C. Hetherington and Robinson [117] improved the method in 1954 by acting on dry sodium nitrite with fluorine.

Nitryl fluoride reacts with sulphuric acid according to the following equation (Hetherington, Hub and Robinson [118]) :

$$NO_2F + H_2SO_4 \rightarrow NO_2^+ + HF + HSO_4^- \quad (44)$$

After that the reaction becomes reversible:

$$HF + 2H_2SO_4 \leftrightarrow HSO_3F + HSO_4^- + H_3O^+ \quad (45)$$

On the basis of eqn. (45) it would be expected that nitryl fluoride in sulphuric acid is a nitrating agent (besides also possessing fluorinating and sulphofluorinating effects).

NITROGEN TRIOXIDE (NITROUS ANHYDRIDE)

Although solid N_2O_3 can exist as a pure compound (m.p. ca. -102°), nevertheless in the liquid phase it very soon begins to dissociate, and exists only at low temperature under an atmosphere containing free nitrogen oxide. At temperatures above -100°C dissociation begins and the gaseous phase is enriched with nitrogen oxide, and the liquid phase with the dioxide. Thus, the "blue-green" liquid commonly described as N_2O_3 is a solution of greater or smaller quantities of NO_2 in N_2O_3.

d'Or and Tarte [119], on the basis of the infra-red spectrum of the compound, have given its constitutional formula as:

$$\begin{array}{l} NO \\ | \\ NO_2 \end{array}$$

(the N-N bond produces an absorption band similar to that given by N_2O_4).

It is assumed that the mechanism of dissociation of nitrogen trioxide involves its separation into disproportionate amounts of the nitrosonium and nitrite ions:

$$N_2O_3 \rightarrow NO^+ + NO_2^- \quad (46)$$

Hence the formation of nitroso compounds (C-nitroso- and O-nitroso, i.e. nitrous acid esters) is possible.

Nitrogen trioxide combines with boron trifluoride to form a complex salt, the structure of which, as assumed by G. B. Bachman and Hokama [104], should be either:

$$(F_3B{\leftarrow}NO_2)^-NO^+ \quad \text{or} \quad (F_3B^+NO)^-NO_2^+$$

In consequence of its dual form the compound can act both as a nitrosating (diazotizing) and as a nitrating agent.

Bachman and Hokama found that benzene was nitrated by the complex in 5-6% yield, whereas nitrotoluene formed gum. If, however, toluene is nitrated in nitroethane, then 56% of *o*- nitrotoluene, 1% of *p*- nitrotoluene and 3% of 2,4-dinitrotoluene are obtained. *o*- Nitrotoluene can be nitrated to 2,4-dinitrotoluene by the complex in 40% yield.

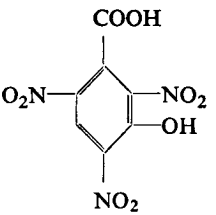
The above mentioned authors have diazotized aniline with the complex and obtained fluorobenzene.

Recently Tedder [120, 121] has shown that by acting directly with the complex on aromatic hydrocarbons, diazonium salts can be obtained.

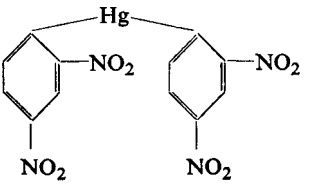
NITRIC ACID IN THE PRESENCE OF MERCURIC NITRATE

The catalytic action of mercuric nitrate in the nitration of anthraquinone with nitric acid was observed in 1906 by Holdermann [122]. Soon after that, Wolffenstein and Boters [123] observed the specific influence that mercuric nitrate exercised on the formation of the products of nitration of benzene. They showed that at a certain concentration of nitric acid, mostly nitrophenols were formed ("oxynitration" reaction).

In his later studies Wolffenstein found that the hydroxyl group could be introduced in this way into the aromatic ring, not only in the case of benzene but also with its derivatives as well. For example, benzoic acid yielded trinitro-m-hydroxybenzoic acid in the presence of mercuric nitrate:

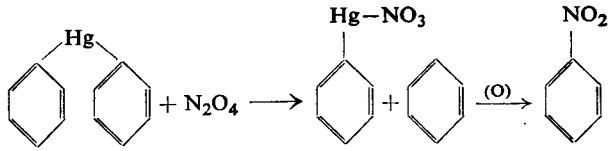


Broders [124] isolated from the nitration products an organomercuric compound to which he ascribed the following formula:



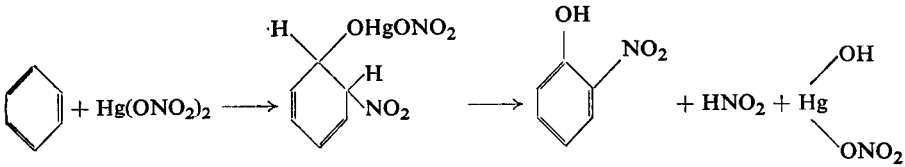
On this basis Desvergnes [125] suggested a mechanism for nitration in the presence of mercuric nitrate that assumes the formation of diphenylmercury as an intermediate product.

Nitrobenzene is also formed besides nitrophenols and this has been explained by Desvergnes according to the following series of reaction:



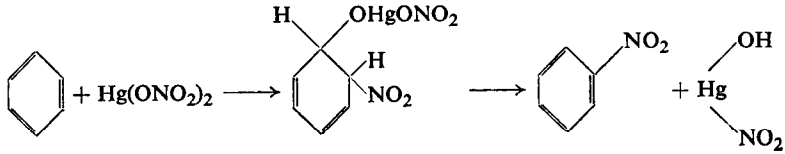
Zakharov [126] criticized Desvergnes's view, which he considered to be inexact in a number of points.

On the basis of his own experiments, Zakharov suggested a different mechanism of reaction. He believed that the catalyst initially weakens the stability of the aromatic ring by the rupture of a double bond on the attachment of mercuric nitrate, e.g.:



(48)

Nitrobenzene would be formed as result of the following reaction:



(49)

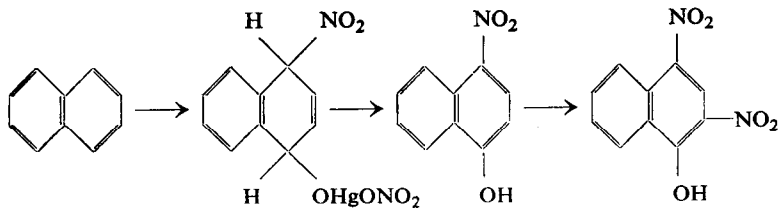
Zakharov found oxynitration to proceed best at 60% concentration of nitric acid.

Davis [127,128] and later Blechta and Patek [129] found that as a result of nitrating toluene in the presence of mercuric nitrate, besides nitrotoluenes, trinitro-*m*- cresol and *p*- nitrobenzoic acid could also be obtained. The authors explained the mechanism of the reaction by assuming the formation of toluene and the mercury salt complex to be the first stage. On decomposition of the complex by the action of nitric acid, the activated hydrocarbon thus formed was nitrated.

According to Kholevo and Eitington [130] the nitratiton of *m*- xylene leads to formation of 4-nitro-3-methylbenzoic acid. Here the mercuric nitrate also enhances the oxidation of the methyl group.

Davis and his co-workers [127,128] found chlorobenzene also undergoes oxynitration by action of 65% nitric acid, with formation of trinitro-m-chlorophenol along with chloronitrobenzenes, while naphthalene when nitrated with more dilute acid, for example, at a concentration of 65%, yielded 2,4-dinitro-a-naphthol besides 2-nitro-a-naphthol.

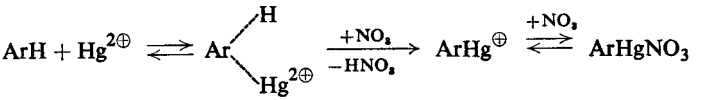
To explain the reaction Davis proposed the following mechanism consistent in the main with Zakharov's view referred to above:



(50)

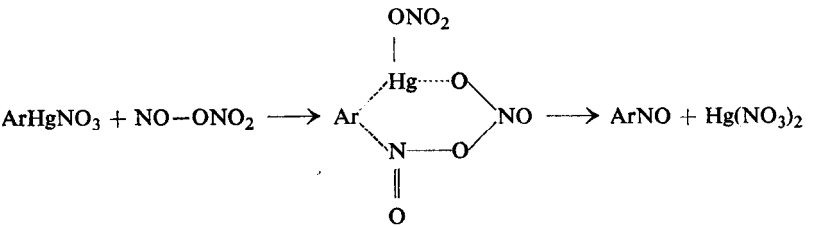
However, the explanation of the reaction, proposed by Titov and Laptev appears to be the most probable and full. Laptev [131] and later Titov and Laptev [71] have suggested that nitration in the presence of mercuric salts proceeds in the following stages:

(1) Formation of a mercury-aromatic compound:



(51)

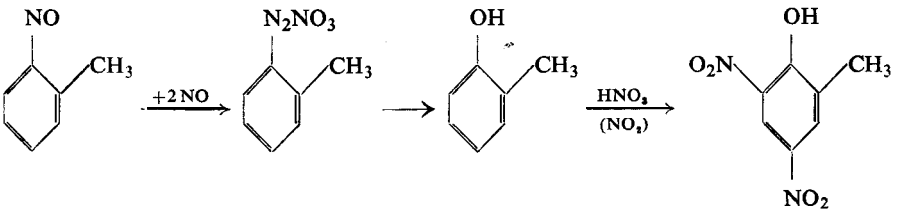
(2) Formation of a nitroso compound by the reaction of the mercury-aromatic compound with N_2O_4:



(52)

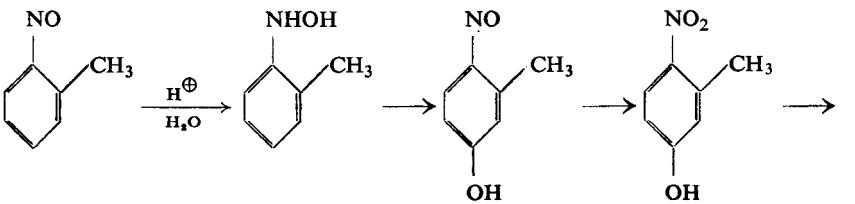
(3) Conversion of the nitroso compound into the nitro compound under the influence of nitrogen oxides and a hydrogen ion.

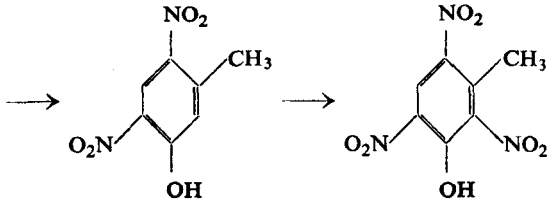
The conversion may consist simply in oxidation or be the result of a more complex reaction. For example, nitrosotoluene can be converted into diazonium nitrate under the influence of nitrous acid. Bamberger [132] found in 1918 that nitrosobenzene could be converted into benzenediazonium nitrate under the influence of nitrous acid. According to Bamberger [133] and Nesmeyanov [134], mercury-aromatic compounds also give nitrates of corresponding diazonium compounds under the influence of N_2O_3, presumably also through nitroso compounds.



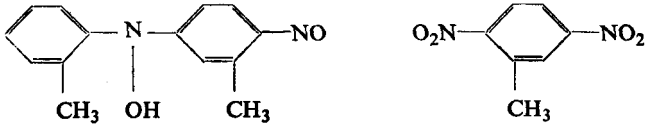
(53)

Titov and Laptev also suggest the possibility of conversions with the aid of the hydrogen ion, causing the reduction of nitroso compounds to hydroxylamine derivatives followed by an oxidation:





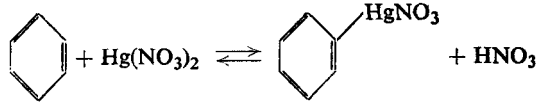
Moreover, diphenylhydroxylamine derivatives and *p*- dinitrotoluene may be formed, e.g. :



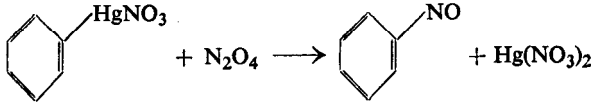
It seems to be certain that the oxynitration reaction in the presence of mercury salts proceeds through the formation of phenylmercuric nitrate. The isolation of phenylmercuric nitrate from a reaction mixture in dilute nitric acid by several authors (Carmack and his co-workers [135], Titov and Laptev [71], and also Broders [124]) favours this view. If an intermediate nitroso compound is formed in the reaction its formation should be ascribed to the reaction between phenylmercuric nitrate and nitrous acid. This view, based on earlier experiments of Baeyer [136], Bamberger [137], Smith and Taylor [137a], has since been confirmed by Westheimer, Segel and Schramm [138], who considered the nitroso compound formed from an organo-mercuric compound to be the principal intermediate product in the Wolffenstein and Böters reaction.

Nitrogen dioxide plays an important role in the reaction. It is this compound that is responsible for the conversion of mercury aryl nitrates into nitroso derivatives.

Westheimer and his co-workers formulated the reaction mechanism in the following way :



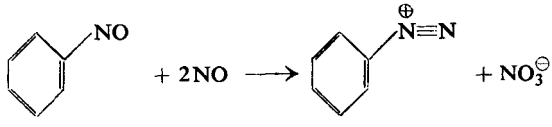
(55a)



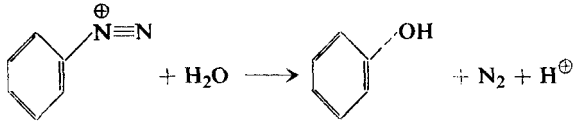
(55b)

The nitrosobenzene formed in the reaction (55b) can then react in either of two ways :

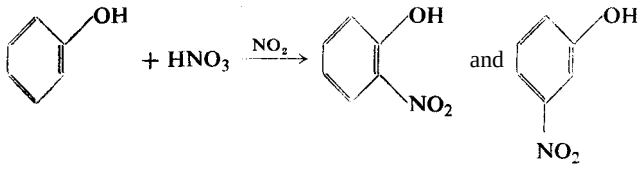
(1)



(55c)

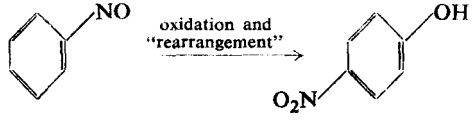


(55d)



(55e)

or (2)

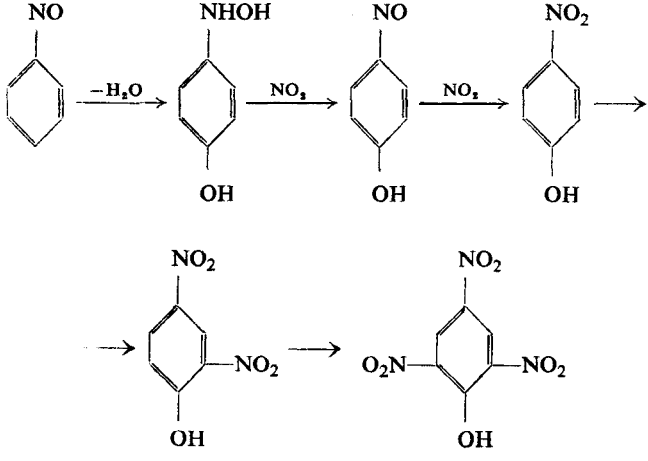


(55f)

The mononitrophenol formed either by the reaction (55e) or by reaction (55f) is, then further nitrated to dinitro- and trinitro-phenols if the concentration of nitric acid is sufficiently high.

Westheimer's formulation of the mechanism of the reaction appears to be the most accurate of all the attempts to elucidate the mechanism of "oxynitration".

Laptev [131] suggested a mechanism based on reactions (55/1) and (55/2), followed by formation of *p*- hydroxyphenylhydroxylamine :



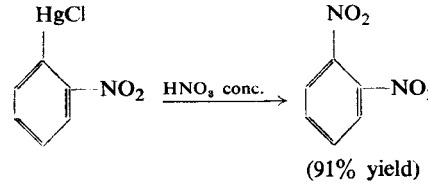
(56)

If nitric acid does not contain nitrogen oxides, a reversible decomposition of the organo-mercuric compound can take place, as has been shown by Baryshnikova and Titov [139]:

$$Ar\text{-}HgNO_3 + HNO_3 \rightarrow Ar\text{-}H + Hg(NO_3)_2$$

At a sufficient concentration of nitric acid, mercury is replaced by the nitro

group. This was shown by Ogata and Tsuchida [40] by means of the following reaction:



(57)

It is rather important to note that if an aromatic nitro compound is the substance being nitrated, addition of mercuric nitrate to the nitric acid has no effect on the reaction. For example, nitrobenzene is nitrated to dinitrobezene in the same yield both in the presence of a mercury salt and in its absence. This can be explained by the fact that nitro compounds such as nitrobenzene do not yield addition product with mercuric salts.

Wright and his co-workers [141] found mercury plus a small amount of aluminium (ca. 2%) and manganese (ca. 5%) to be a more efficient catalyst than mercury alone. The experiments have shown that mercury increases the reaction rate while manganese, though it has no influence on the principal reaction, assists in the complete oxidation of oxalic acid which would otherwise contaminate the reaction product.

It is of interest to point out the observation of the above authors that addition of copper and especially vanadium inhibits the reaction.

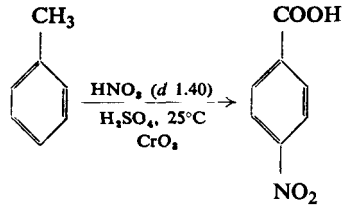
McKie [142] found the yield of the nitration product to be higher when mercuric nitrate was present in nitric acid. Thus for example, phenanthrene, when nitrated with anhydrous nitric acid in the presence of $Hg(NO_3)_2$, gave nitrophenanthrene in a yield higher by 13% than when nitric acid alone had been used. Likewise the yields of nitro derivatives of phenol and α– naphthol could be increased by addition of mercuric nitrate to dilute nitric acid.

Numerous industrial studies have been carried out to investigate the possibility of using the oxynitration method for the commercial production of picric acid. However, they have failed to provide a reliable method for industrial application. Particulars on some experiments on the industrial scale are dealt with in the chapter on nitro derivatives of phenol.

NITRATING MIXTURES WITH STRONG OXIDIZING AGENTS

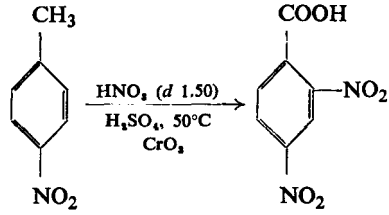
T. Urbanski, Semenczuk *et al.* [143] developed a method of "nitroxidation" that consists in nitrating an aromatic hydrocarbon which contain an aliphatic side chain, using nitrating mixtures containing strongly oxidizing agents, such as CrO_3.

Toluene can be nitrated to yield *p*- nitrobenzoic acid and *p*- nitrotoluene to yield 2,4-dinitrobenzoic acid :



(58)

(30% yield)



(59)

(60% yield)

NITROUS ACID AS A NITRATION CATALYST AND AS A NITRATING AGENT

The name "nitrous acid" is usually applied to substances which give HNO_2 when dissolved in water. Thus not only is N_2O_3 a nitrous acid anhydride, but so also is nitrogen dioxide, which, as is known, may be regarded as a mixed nitrous-nitric anhydride.

Ingold and his co-workers [144] present the dissociation of nitrogen dioxide and nitrous anhydride in the following way:

$$2N_2O_4 + H_2O \leftrightarrow N_2O_3 + 2HNO_3 \quad (60)$$

$$NO + NO_2 \leftrightarrow N_2O_3 \leftrightarrow NO^+ + NO_2^- \quad (61)$$

The nitrous ion NO_2^- attracts a proton, thus facilitating the nitrosating action of the nitrosonium ion NO^+.

In his work on the nitration kinetics, which has already been referred to, Martinsen [145] found that in the nitration of phenol with nitric acid, nitrous acid, if present, acted as a catalyst on the nitration process. The presence of nitrous acid was necessary for initiating the reaction, further quantities being formed in the reaction of oxidation of phenol with nitric acid, which accompanied the nitration reaction. Thus the reaction of nitrating phenol is an autocatalytic one.

Amall [146] inferred from his investigations on the nitration of phenol in an alcoholic or acetic acid solution that nitrous acid was formed only initially as a result of side reactions and then the following reactions took place:

$$HNO_3 + HNO_2 \rightarrow N_2O_4 + H_2O \quad (62)$$

$$C_6H_5OH + N_2O_4 \rightarrow NO_2.C_6H_4.OH + HNO_2 \quad (63)$$

On the basis of Arnall's experiments, Zawidzki [147] had deduced the following equation for the rate of phenol nitration:

$$\frac{dx}{dt} = k(a-x)(b-x)(c-x)$$

where x is the concentration of nitrophenol just being formed; a, b, c are the initial concentrations of phenol, nitric acid and nitrous acid respectively: (a-x), (b-x), (c-x) are the concentrations of these compounds after the lapse of time t. The reaction rate constant equals k = ca. 0.043.

Klemenc and Schüller [148] have derived the following formula for the rate of nitration (v) with nitric acid:

$$V = k[HNO_3]^{5/2} [HNO2]^{1/2} c^2$$

where c is the concentration of the compound being nitrated.

It can be seen from this equation that nitrous acid as an agent increasing the reaction rate is of great importance.

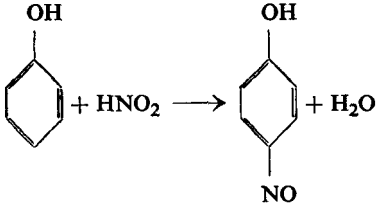
Kartashev [149] has investigated the reaction of phenol with nitric acid in detail. The author assumes the mechanism of the nitration of phenol with nitric acid to be as follows:

(1) In the first stage nitric acid oxidizes phenol and forms nitrous acid.

(2) Nitrous acid reacts with phenol to form nitrosophenol.

(3) Nitrosophenol is oxidized by nitric acid to nitrophenol forming again new quantities of nitrous acid.

$$HNO_3 \rightarrow HNO_2 + O \qquad (64)$$



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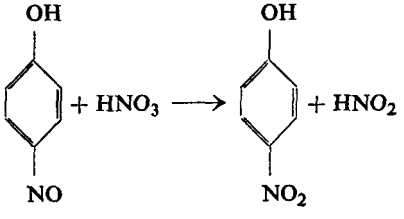


(66)

It has been shown that the addition of nitrous acid lowers the initiation temperature of the reaction; the addition of *p*- nitrosophenol affects the reaction in a similar way. The addition of urea to nitric acid results in lowering the reaction rate. A similar nitration scheme was given by Veibel [150].

Cohen and Wibaut [151] in their work, already mentioned (p. 44), on the nitration of aromatic hydrocarbons with a mixture of nitric acid and acetic anhydride, confirmed the catalytic action of nitrous acid in this case too. As the reaction proceeded the concentration of nitrous acid increased owing to the oxidizing action of nitric acid on the hydrocarbon.

Titov [34] proved, after having investigated a large group of aromatic compounds, including phenols, naphthalene, etc. that pure nitric acid (d 1.40) free from nitrous acid had no nitrating properties at all. The true nitrating agent, the author believed, was NO_2, as mentioned before. Titov's scheme is as follows:

$$ArH + NO_2 \longrightarrow Ar\begin{matrix}H\\NO_2\end{matrix} \xrightarrow{NO_2} ArNO_2 + HNO_2 \qquad (67)$$

lngold and his co-workers [152] when investigating the nitration of phenols and their ethers, came to the conclusion that it was the nitrosonium ion, NO^+, formed as a result of the hypothetical reactions (a) and (b):

$$HNO_2 + HNO_3 \leftrightarrow H_2NO_2^+ + NO_3^- \qquad (a)$$

$$H_2NO_2^+ \leftrightarrow NO^+ + H_2O \qquad (b)$$

$$NO^+ + NO_3^- \leftrightarrow N_2O_4 \qquad (c)$$

that had initiated nitration reactions, eqn. (c) deriving from eqns (a), and (b).

The nitrosonium ion may react according to the equation:

$$ArH + NO^+ \rightarrow ArHNO^+ \rightarrow ArNO + H^+ \qquad (68)$$

the nitroso compound formed being rapidly oxidized to a nitro compound:

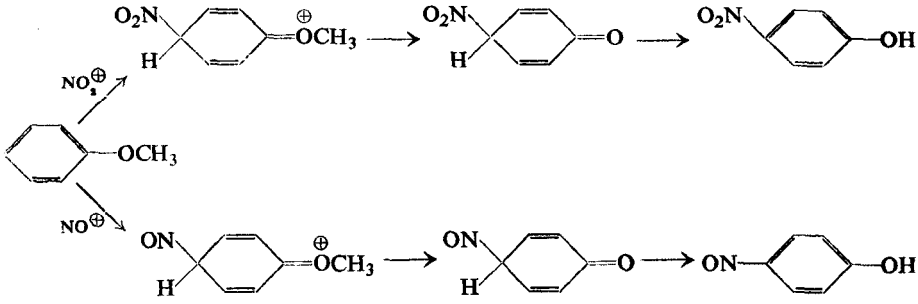
$$ArNO + HNO_3 \rightarrow Ar\text{-}NO_2 + HNO_2 \qquad (69)$$

Schramm and Westheimer [153] have observed that when a phenyl ether such as anisole is nitrated, the presence of nitrous acid is also necessary. The authors believed nitrosoanisole was formed as an intermediate product as in the nitration of phenol. Their assumption was based on the fact that *p*- nitrosoanisole yields nitration products identical to those given by anisole, viz. nitroanisoles and 2,4-dinitrophenol. Thus, beside the nitration, a partial break-down of the ether bond takes place.

A partial dearylation of diarylether during nitration had already been observed by Reilly, Drumm and Barrett [154]. The dealkylation, observed by Schramm and Westheimer, has been confirmed by Ingold and his co-workers [152]. For example *p*- chloroanisole, when nitrated with a 6N solution of nitric acid in the presence of acetic acid at 20°C gave 4-chloro-2-anisole in 66% yield and 4-chloro-2,6-dinitrophenol in 33% yield of theory.

Simultaneously the methyl group, after being split off from *p*- chloroanisole,

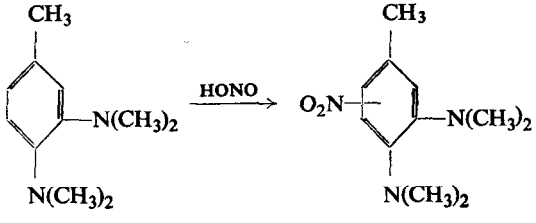
formed methyl acetate. Cook and Bunnett [155] have tried to explain the phenomenon of splitting off the methyl group as the result of the formation of a transient oxonium ion, which, as is known, is able to give off an alkyl radical:



On the other hand Ingold and co-workers [144,155a] have proved that the presence of nitrous acid in the nitrating acid decreases the rate of nitration of aromatic compounds in general with the exception of phenols. The same holds true for phenyl ethers (e.g. anisole) which are more difficult to nitrate with higher concentrations of nitric acid in acetic acid (e.g. 8N) in the presence of nitrous acid, whereas with a less concentrated nitric acid (e.g. 5N), nitrous acid accelerates the reaction.

Nitrous acid itself can act as a nitrating agent. This was noticed for the first time by Niementowski [156] and Koch [157].

Niementowski reacted sodium nitrite with a solution of 3,4-bis(dimethylamine)-toluene in acetic acid and obtained a nitro derivative:



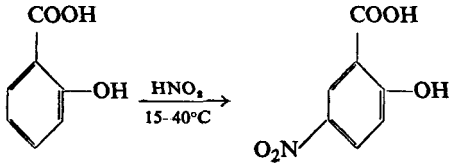
(70)

m. p. 63°C

Similarly Koch prepared chloronitrodimethylaniline by acting with a stoichiometric quantity of sodium nitrite on an acid solution of *p*- chlorodimethylaniline. Pinnov and Schuster [158] confirmed his results.

A number of other authors have also nitrated aromatic amines, acting with sodium nitrite on the amine dissolved in hydrochloric or acetic acid. Thus, triphenylamine and its methyl derivative in acetic acid were nitrated by Häussermann and Bauer [159], and Rupe, Braun and Zembruski [160] and Tsuruta and Oda [161] nitrated derivatives of dimethylaniline in hydrochloric acid to yield mononitro products.

Deninger [162] discovered that salicylic acid can be nitrated with nitrous acid to yield mononitrosalicylic acids :



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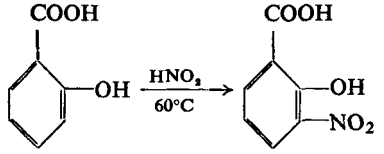

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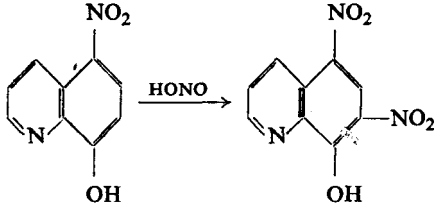
T. Urbanski and Kutkiewicz [70] found that 5-nitro-8-hydroxyquinoline, when boiled with a solution of sodium nitrite in 10% hydrochloric or sulphuric acid, yielded 5,7-dinitro-8-hydroxyquinoline:



(73)

The sodium nitrite is used in an excess. The yield of dinitro-8-hydroxyquinoline obtained amounts to about 30% (cf. also the reaction 7, p. 85). The mechanism of this reaction cannot consist in the formation of a nitroso compound which would be oxidized to a nitro compound, as no nitrosation of a nitrophenol is known.

NITROUS ACID IN THE PRESENCE OF HYDROGEN PEROXIDE

Hydrogen peroxide reacts with nitric and nitrous acids to form the corresponding pernitric acids, of which pernitrous acid is a better defined compound. Baeyer and Williger [163] reported the possibility of obtaining it by reacting ethylhydroperoxide with alkyl nitrate. Raschig [164] has studied the action of hydrogen peroxide on nitrous acid and found such a mixture to be a more powerful oxidizing agent than each of the components taken separately.

Raschig was not correct in ascribing the structure of pernitric acid, HNO_3, to the product of reaction of H_2O_2 with HNO_2. Schmidlin and Massini [165] have proved it to be a pernitrous acid HO-ONO. Extensive studies on pernitrous acid have been carried out by Trifonov [166], who found that hydrogen peroxide when reacted with nitrous acid formed the peroxide, N_2O_6, which gave nitrous acid under the influence of water, the solution appearing yellow for a while.

Kortüm and Finckh [I67] found the absorption spectrum of the yellow solution was similar to that of the nitrate ion, showing however some difference.

The kinetics of the reaction of nitrous acid with hydrogen peroxide have been

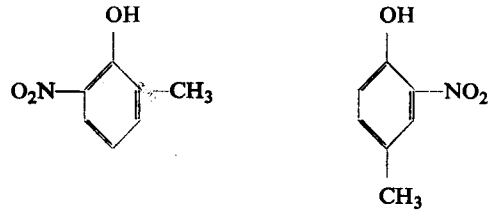
studied by Shills, Rybakov and Pal [168], Shilov and Stepanova [169] and Halfpenny and P. L. Robinson [170].

The experiments so far performed have sometimes been contradictory, but they have led to the conclusion that pernitrous acid does exist.

Nitration with pernitrous acid. The first investigations into the nitration of benzene with per-nitrous acid were performed by Trifonov [166]. In 1922 he found *o*- nitrophenol to be the reaction product and suggested the application of the reaction for detecting benzene and other aromatic hydrocarbons. His results were confirmed by the experiments of Halfpenny and P. L. Robinson [170].

It has been shown that aromatic hydrocarbons can be nitrated by pernitrous acid even at very low acid concentrations (e.g. 2%) at room temperature. The hydroxylation of the hydrocarbon takes place simultaneously in many cases. A characteristic feature of the reaction is that the nitro group mostly takes the *meta* position with respect to the substituent already present. If a nitro and a hydroxyl group are introduced simultaneously the hydroxyl group nearly always takes the *ortho* or *para* position with respect to the substituent already present. Diphenyl derivatives are also formed.

Toluene also yields nitro derivatives of *o*- and *p*- cresol besides nitrotoluenes and benzaldehyde :

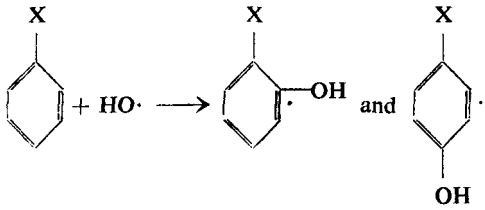


Nitrobenzene gives *m*- dinitrobenzene along with small quantities of the *ortho*- and *para*- isomers, a mixture of *o*-, *m*- and *p*- nitrophenols and a small quantity of 3,3'-dinitrodiphenyl.

Chlorobenzene is converted mainly into *m*- chloronitrobenzene and *o*- chlorophenol and 2-nitro-4-chlorophenol are also formed.

The yield of nitro compounds is, however, not high and does not generally exceed 10%. The method is therefore not of practical importance as yet, although it is interesting from the theoretical point of view. A high dilution of nitrous acid during nitration provides evidence that the nitronium ion cannot be the nitrating agent in the reaction. Halfpenny and Robinson assume the nitration does not take place through nitrosation and oxidation as in the case of nitrophenols (p. 117), and they advance the hypothesis that the nitrating action of pernitrous acid consists in the formation of a free aromatic radical, which reacts with nitrogen dioxide, split off from the pernitrous acid:

$$HOONO \rightarrow HO^{*} + {}^{*}NO_2 \qquad (74)$$



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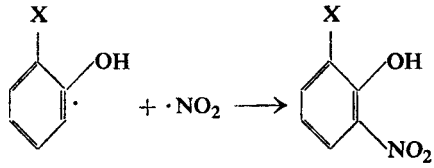


(76)

Nitrous esters can react with alkyl peroxides to yield alkyl nitrates [163,221] (see also Vol. II).

ORGANIC COMPOUNDS AS NITRATING AGENTS

NITRIC ACID ESTERS

Nitric acid esters can be used as nitrating agents in the presence of sulphuric acid and in some cases in a strongly alkaline medium.

Nitric esters in mixtures with sulphuric acid. Raudnitz [171] was the first to draw attention to the nitrating properties of solutions of ethyl nitrate in sulphuric acid. Later in 1941, Titov [34] expressed the view that such a solution contains the nitronium ion, and L. P. Kuhn (p. 15) proved this by cryometric measurements. A solution of ethyl nitrate in sulphuric acid has been used for nitrating aromatic compounds.

The application of other nitric acid esters is also possible. Thus, Bucherer [172] suggested the use of a solution of nitrocellulose in sulphuric acid to nitrate benzene to nitrobenzene, while Plaiek and Ropuszyliski [173] suggested solutions of nitric esters of polyalcohols, such as nitroglycerine, nitromannite, pentaerythritol tetranitrate, for nitration of aromatic hydrocarbons. Ropuszyliski [174] recently investigated the action of a solution of nitroglycerine in sulphuric acid more fully and inferred that decomposition of nitroglycerine by sulphuric acid to form a nitronium ion was probably taking place by stages:

$$C_3H_5(ONO_2)_3 + H_2SO_4 \text{ <-> } C_3H_5(ONO_2)_3H^+ + HSO_4^- \quad (77)$$

$$C_3H_5(ONO_2)_3H^+ \text{ <-> } C_3H_5(OH)(ONO_2)_2 + NO_2^+ \quad (77a)$$

With an excess of sulphuric acid, glycerine dinitrate was decomposed to give further nitronium ions, etc. Finally a double ester nitric and sulphuric of glycerol was formed :

$$C_3H_5(OH)_2(ONO_2) + H_2SO_4 \text{ -> } C_3H_5(OH)(ONO_2)(OSO_3H) + H_2O \quad (77b)$$

Nitric esters in alkaline medium. In some instances compounds containing an active methylene group can be nitrated with nitric esters in the presence of

sodium alcoholates. This is a generally known method for obtaining phenylnitromethane from benzyl cyanide (Wislicenus and Endres [175] ; Meisenheimer [175a]).

The reaction proceeds as follows:

$$C_6H_5CH_2 + C_2H_5ONO_2 + C_2H_5ONa \rightarrow C_6H_5C{=}NOONa + 2C_2H_5OH \qquad (78)$$

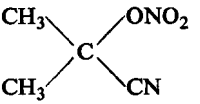
(CN) (CN)

$$C_6H_5C{=}NOONa \xrightarrow{NaOH} C_6H_5C{=}NOONa \xrightarrow{H^+} C_6H_5C{=}NOOH$$

(CN) (COONa) (COOH)

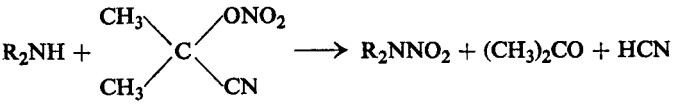
$$C_6H_5CH_2NO_2 \leftarrow C_6H_5CH{=}NOOH \quad (-CO_2) \qquad (78a)$$

The use of acetone cyanohydrin nitrate has recently been proposed for reactions of this type:



(Anbar, Dostrovsky, Samuel and Yoffe [176]; Emmons [177]; Emmons and Freeman [178]).

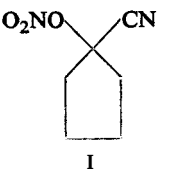
The advantage of this compound over simple alcohol esters is that the O-N bond is weakened by the highly electronegative nitrile group. Besides, the compound does not contain α– atoms of hydrogen and in this way the oxidation to an aldehyde or ketone by the NO_2 groups can be avoided. According to Emmons, McCallum and Freeman [179], this reagent has proved to be particularly useful in the nitration of amines:



$$R_2NH + \text{(reagent)} \longrightarrow R_2NNO_2 + (CH_3)_2CO + HCN \qquad (79)$$

The yield amounts to 80% for the nitration of secondary amines, and 60% for primary ones.

Nitrates of cyclopentanone or cyclohexanone cyanohydrin (I and II) may also be nitrating agents.



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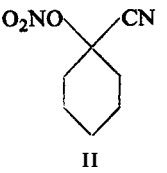


II

ACYL NITRATES (MIXED ANHYDRIDES)

Acyl nitrates are rather powerful nitrating agents. The simplest of them, acetyl nitrate, CH_3COONO_2 (b. p. 22°C at 70 mm Hg), is formed by reacting acetic anhydride with N_2O_5. It is presumably present in nitrating mixtures consisting of nitric acid and acetic anhydride (Pictet and Khotinsky [180]). The aromatic hydro-

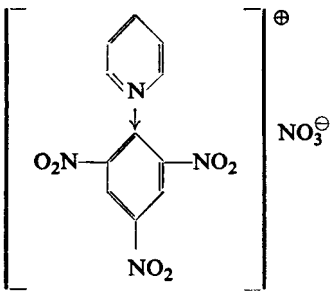
carbons are nitrated to mononitro derivatives in a yield close to theoretical. Toluene was nitrated to a mixture of 88% of *o*- and 12% of *p*- nitrotoluene and phenol to a mixture of 51% *o*- and 48% *p*- nitrophenol. Mononitro compounds are not nitrated further to dinitro derivatives by acetyl nitrate.

Benzoyl nitrate $C_6H_5COONO_2$ (prepared by reacting silver nitrate with benzoyl chloride) can in certain cases be a useful nitrating agent (Francis [181]). For example, thiophene is nitrated with this compound in theoretical yield, while if conventional methods are used, only a low yield is obtained and this only with great difficulty.

NITRATES OF SOME ORGANIC BASES

Battegay and Brandt [181a] succeeded in nitrating anthracene to 9-nitroanthracene with 70% yield by heating anthracene with pyridine nitrate and excess of pyridine to 125°C. Naphthalene was nitrated to a-nitronaphthalene (40% yield) at 130°C in presence of zinc chloride.

Okoli [181b] has prepared picrylpyridinium nitrate I by acting on picrylpyridinium chloride with nitric acid or metal nitrates:



I (m.p. 103-105°C)

Okon and Hermanowicz [181c] have found that the nitrate I can serve as a nitrating agent.

Thus the authors prepared α– nitronaphthalene from naphthalene with the yield of 80% by warming I with naphthalene. In a similar way toluene was nitrated at 80°C to 2,4-dinitrotoluene (yield 65%). By warming chloroform with I at 40-50°C chloropicrine resulted with the yield of *ca.* 30%.

ALIPHATIC NITRO COMPOUNDS

Some nitro compounds (C-nitro compounds and nitramines-N-nitro compounds) can serve as nitrating agents.

Tetranitromethane and hexanitroethane

In the presence of alkalis, tetranitromethane shows nitrating properties. This is explained by the fact that alkalis decompose it by splitting off the nitro group and giving rise to nitroform (more exactly to its salt), according to the reaction (Hantzsch and Rinckenberger [182]) :

$$C(NO_2)_4 + 2KOH \rightarrow KNO_3 + KC(NO_2)_3 + H_2O \qquad (80a)$$

Apart from this, other, more complex side reactions take place, involving oxidation-reduction processes and a complete decomposition of the substance with the formation of nitrite and CO_2 (E. Schmidt [183]) :

$$C(NO_2)_4 + 6KOH \rightarrow 4KNO_2 + K_2CO_3 + 3\ H_2O \qquad (80b)$$

The main reaction may be expressed by the equation:

$$C(NO_2)_4 + KOH \rightarrow KC(NO_2)_3 + HNO_3 \qquad (80c)$$

in which the transient formation of nitric acid is acknowledged.

Nitration with tetranitromethane is carried out mostly in the presence of pyridine which with nitroform forms a crystalline addition product.

Hexanitroethane may be used as a nitrating agent in a similar way (for example, Alsop and Kenner [184]).

Nitroguanidine

Davis and Abrams [184a] have observed that aromatic compounds easy to nitrate such as phenol, acetanilide, etc. can be nitrated by a freshly prepared solution of nitroguanidine in sulphuric acid.

There is no evidence that a solution of nitroguanidine in sulphuric acid contains free nitric acid, although the solution turns diphenylamine blue and reacts with mercury, thus behaving identically like nitric acid. It is estimated that nitric acid can be formed only in the presence of compounds that are readily nitrated.

According to this view, nitroguanidine decomposes in the presence of sulphuric acid to give nitramine (eqn. 81), which is hydrolysed in the presence of substances convertible to nitro compounds to form ammonia and nitric acid (eqn. 81):

$$NH_2\text{-}\underset{\underset{\|}{\mathbf{NH}}}{\overset{\overset{\|}{\mathbf{NH}}}{\mathbf{C}}}\text{-}\mathbf{NHNO_2} \rightarrow \mathbf{NH_2NO_2} + \mathbf{NH_2CN} \qquad (81)$$

$$\mathbf{NH_2NO_2} + \mathbf{H_2O} \rightarrow \mathbf{NH_3} + \mathbf{HNO_3} \qquad (82)$$

The presence of cyanamide, NH_2CN, in the solution after nitration, as stated by Davis and Abrams, may serve as evidence confirming the above view.

More convincing, however, is the hypothesis that in nitroguanidine, under the influence of sulphuric acid, a loosening of the nitrogen atoms bond takes place, and a nitro group in the form of a nitronium ion breaks off:

$$NH_2\text{-}\underset{\underset{\|}{NH}}{\overset{\overset{\|}{C}}{}}\text{-}NH\text{-}NO_2 \rightarrow NH_2\text{-}\underset{\underset{\|}{NH}}{\overset{\overset{\|}{C}}{}}\text{-}NH\text{-} + NO_2^+ \qquad (83)$$

Some of the primary nitramines have similar properties and can act as nitrating agents. However, no systematic studies on the subject have been reported in the literature as yet.

NITRATION UNDER INFLUENCE OF GAMMA RADIATION

It has recently been found by Mint and his co-workers [185] that nitration of benzene occurs when benzene in an aqueous solution of calcium nitrate is irradiated with gamma rays. The yield is up to 45% of nitrobenzene and a certain amount of picric acid is also formed. Mint suggested the formation of the nitronium ion. through the following sequence of reactions:

$$NO_3^- + H \rightarrow NO_2^- + OH \rightarrow NO_2 + OH^- \quad (a)$$

$$NO_2 + OH \rightarrow NO_2^+ + OH^- \quad (b)$$

Nitration would proceed as (c) in accordance with the radical mechanism or as (d) assuming an ionic mechanism:

$$*C_6H_5 + NO_2 \rightarrow C_6H_5NO_2 \quad (c)$$

$$C_6H_6 + NO_2^+ \rightarrow C_6H_5O_2 + H^+ \quad (d)$$

The radical, $*C_6H_5$, would be formed through the reaction between benzene and OH or HO_2 radicals.

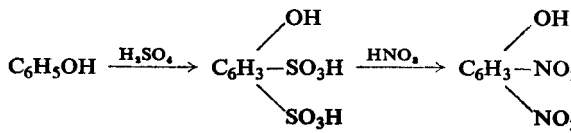
Falecki, Mint, Slebodziliski and T. Urbanski, [185a] have also found that paraffin hydrocarbons dissolved in dinitrogen tetroxide are nitrated at 28°C when they are subjected to irradiation with gamma rays. The yield for n-hexane was up to 15% of non-gaseous products of both nitration and oxidation. The characteristic feature of the reaction differentiating it from nitration at elevated temperature described above (p. 94) is the fact that no pyrolysis of the hydrocarbon occurs, and therefore long chain paraffins are not so readily split into shorter fragments as it occurs at high temperature. The authors also found that n-hexane reacts with dinitrogen tetroxide at 28°C without irradiation. However, the yield of non-gaseous products is lower ***(ca.*** 8%) and the products containing nitrogen are mainly nitrous esters. This would suggest that N_2O_4 probably forms ions NO_2^+ or $*NO_2$ radicals under the action of irradiation. Without irradiation a considerable amount of nitrite ions ONO^- are present and these are responsible for the formation of nitrous esters.

INDIRECT METHODS OF INTRODUCING A NITRO GROUP

It has already been mentioned (p. 5) that indirect methods of introducing a nitro group are used in many cases.

SUBSTITUTION OF SULPHONIC GROUPS

Sulphonation of compounds followed by substituting the sulpho group by a nitro group is the method of great practical importance. This method is widely used for the nitration of phenols. The reaction occurs as follows:



(84)

Owing to this course of the reaction the oxidation of phenols and the formation of side-products can be largely avoided. This is discussed in more detail in the chapter on the nitration of phenols (p. 502).

Another method, of great importance in laboratory practice, is the substitution of a halogen by a nitro group.

SUBSTITUTION OF HALOGEN

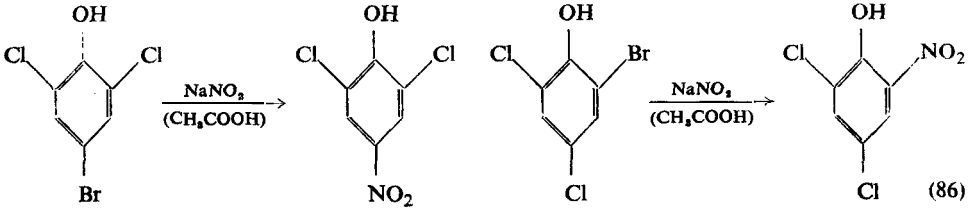
In laboratory methods for the preparation of aliphatic nitro compounds, the V. Meyer reaction [186] consisting in reacting alkyl iodides or bromides with silver nitrite, is widely used. As is well known, the reaction can proceed in two directions, resulting in the formation of a certain quantity of a less stable nitrous ester besides a nitro compound. Instead of silver nitrite mercuric nitrite may be used (Ray[187]).

Kornblum and his co-workers [188, 188a] have recently improved the method used for the preparation of nitroparaffins with longer aliphatic chain (over C_8). They reacted an alkyl chloride with sodium nitrite in the solvent (dimethylformamide) for several hours at low temperature, obtaining a homogeneous solution:

$$RCH_2Cl + NaNO_2 \rightarrow RCH_2NO_2 + NaCl \qquad (85)$$

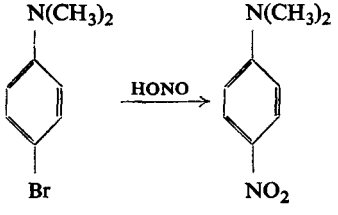
The addition of urea to the reacting system prevents side reactions, e.g. the formation of nitrous esters. The yield amounts to about 60%.

In aromatic compounds such a reaction is possible only in the case of polybromo- or polyiodo-derivatives of phenol. Sodium nitrite and acetic acid may be used for replacing one of the Br or I atoms by the nitro group (Zincke [189], Raiford [190-193]):



(86)

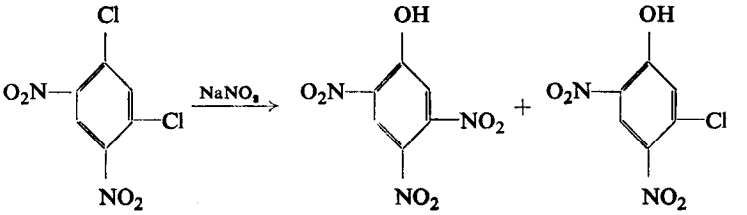
Not only salts of nitrous acids but also nitrous acid itself can replace halogen by the nitro group. This has been discovered by Wuster and Scheibe [194] when they reacted sodium nitrite with bromodimethylaniniline in hydrochloric acid:



(87)

In addition, a certain quantity of bromonitrosodimethylaniline was formed.

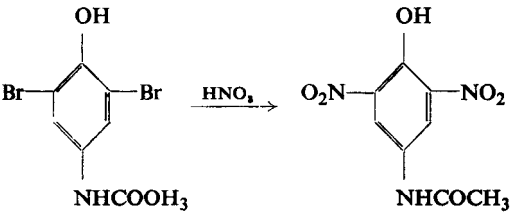
An interesting case of introducing the nitro group, accompanied by hydrolysis, was reported by Leandri [195] :



(88)

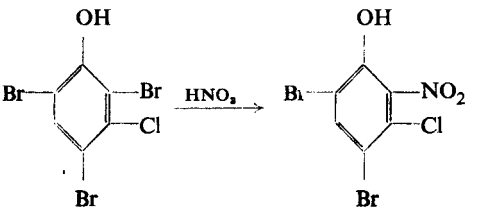
When halogenated phenols or phenolic ethers are nitrated with nitric acid a halogen *o*- or *p*- to hydroxyl or alkoxyl group can also be replaced. The ease of replacement appears to be in the order Cl< Br<I.

A typical and the oldest example was given by P. W. Robertson [195a]:



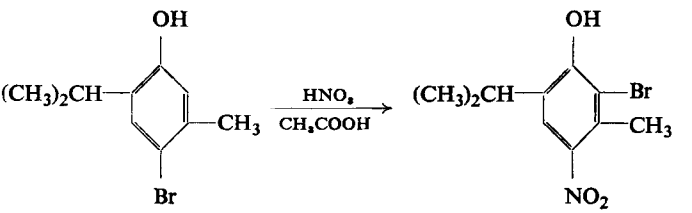
(89)

Hodgson and Smith [196] give an example which indicates the mobility of various halogen atoms:



(90)

Sometimes the free halogen liberated in this displacements itself enters the aromatic ring, thus giving rise to an apparent substitution. Thus P. W. Robertson [196a] and P. W. Robertson and Briscoe [196b] found that 6-bromothymol on nitration in dilute acetic acid gives 2-bromo-6-nitrothymol:

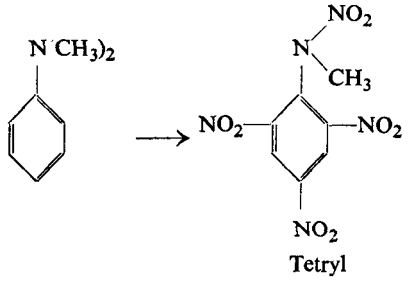


(91)

Aliphatic nitro compounds may be obtained in the well known Kolbe reaction [197] by acting with sodium nitrate on α– halogen fatty acids. During the substitution the carboxyl group splits off.

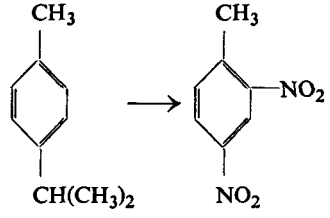
OTHER NITRATION REACTIONS BY SUBSTITUTION

An alkyl group is sometimes replaced by a nitro group. This happens particularly when nitrating amines to nitramines. As a classical example, the formation of trinitrophenylmethylnitramine (tetryl) from dimethylaniline can be mentioned: (Vol. III)



Tetryl (92)

Some branched alkyl groups, especially the isopropyl group, can readily be replaced by a nitro group, even when they are attached to an aromatic ring. For example, under certain nitration conditions thymol ethers can yield the corresponding trinitro-m-cresol ethers (Giua [198]). Similarly, the nitration of *p*- cymene may lead to dinitrotoluene (Alfthan [199]):



(93)

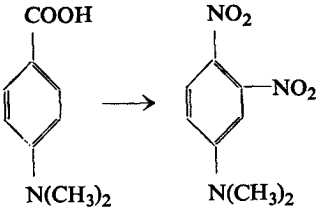
The nitration reaction that consists in replacing a hydroxyl group by a nitro group is not often used. It is usually applied to tertiary alcohols. For example, tert-butyl alcohol (trimethylcarbinol) reacted with nitric acid to yield tert-nitrobutane in 10% yield in relation to the alcohol weight (Haitinger [4]):

$$(CH_3)_3COH \xrightarrow{HNO_3} (CH_3)_3CNO_2 \qquad (94)$$

In the aliphatic series the substitution of a carboxyl group by a nitro group can only be accomplished with a small yield. gem-Dinitropropane, for example, is obtained from isobutyric acid (Bredt [200]):

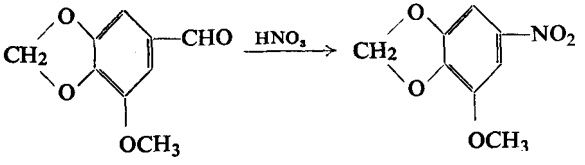
$$(CH_3)_2CHCOOH \xrightarrow{HNO_3} (CH_3)_2C(NO_2)_2 \qquad (95)$$

In the aromatic series such a reaction is more often observed. For example, *p*- dimethylaminobenzoic acid can be nitrated to 2,4-dinitrodimethylaniline (Reverdin [201]) :



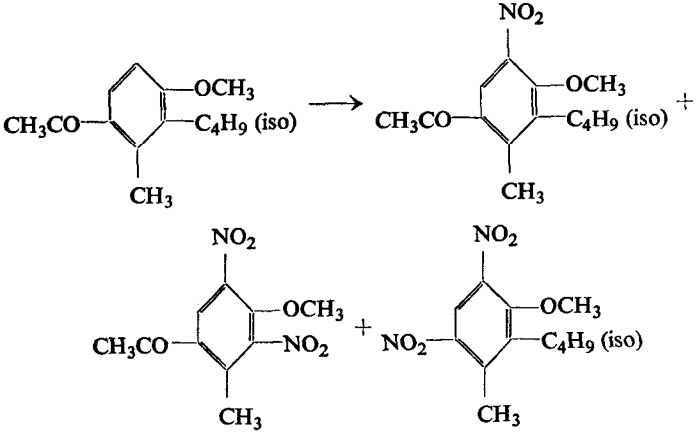
(96)

An aldehyde group can be replaced by a nitro group as shown by Salway [202] and Harding [202a]:



(97)

A ketone group can also be replaced by a nitro group along with an alkyl group (Barbier [203]) :

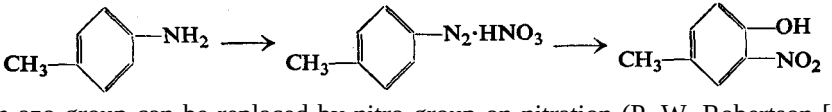


(98)

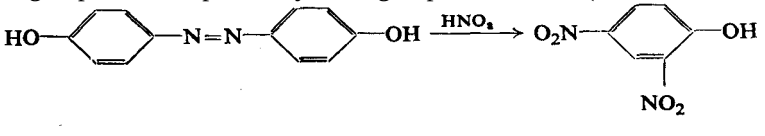
A new type of substitution of the chloromercuric group described by Ogata and Tsuchida [140] has been already mentioned (p. 118).

The substitution of a primary amino group by a nitro group generally occurs by diazotization and the Sandmeyer reaction. ("Körner and Contardi reaction") [222].

In certain cases, diazonium salt nitrates, when boiled in aqueous solution, are converted to nitrophenols. For example p-toluidine, when diazotized in nitric acid solution, forms nitro-p-cresol after the solution had been brought to the boil (Nölting and E. Wild [203a]):

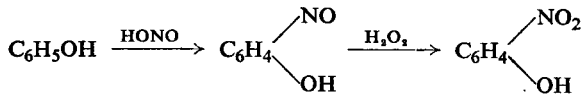


An azo group can be replaced by nitro group on nitration (P. W. Robertson [204])



INTRODUCING THE NITRO GROUP BY OXIDATION

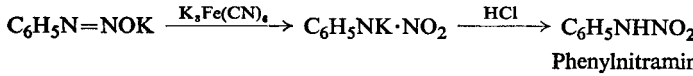
In addition to the nitration of phenols by substitution of sulpho groups (p. 130) the method of nitrosation of phenols, followed by oxidation of the nitroso to the nitro group has some practical application:



(101)

The method is used for those readily nitrated phenols (e.g. resorcinol), when less nitro groups are to be introduced than is possible in the direct nitration (Kostanecki and Feinstein [205]).

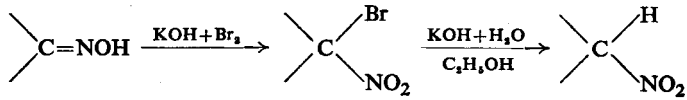
Oxidation of diazo compounds may result in the formation of nitramines, for example, phenylmtramine :



(102)

This is one of the reactions which were used to prove that nitramines are compounds with the nitro group attached to the nitrogen atom.

A nitro group may also be introduced by the oxidation of oximes. For this, salts of hypobromous acid are generally used. This method is sometimes applied for the preparation of aliphatic nitro compounds. The reaction proceeds in the following way (Forster [206], Cherkasova and Mehrikov [207], Iffland *et al.* [208]):



(103)

Iffland and Criner [209] have improved the method. They obtained nitrocyclohexanone from cyclohexanone in about 50% yield, using N-bromosuccinimide as an oxidizing and brominating agent.

Introducing a nitro group by oxidation of a primary amino group. The method of oxidizing a primary amino group to a nitro group is sometimes used commercially. A nitroso compound is an intermediate product of the reaction and it can generally be isolated :

$$-NH_2 \quad -> \quad -NO \quad -> \quad -NO_2$$

The oxidation is carried out by means of the so-called Caro's acid (H_2SO_5), which is prepared by reacting sulphuric acid with persulphuric acid salts, or by reacting concentrated hydrogen peroxide with sulphuric acid.

In this way nitrosobenzene may be obtained from aniline, as has been shown by Bambergcr and Tschirner [220]. Nitrosobenzene may then be oxidized to nitrobenzene.

Page and Heasman [210] obtained 3,6- (or 2,5-) dinitrotoluene by reacting Caro's acid with 5-nitro-o-toluidine. Brady and Williams [211] used the same method

for the preparation of 2,3,4- and 2,4,5-trinitrotoluencs from 3,4- or 4.5-dinitro-o-toluidine. Holleman [211a] also used this method for the last stage of the preparation of tetranitrotoluene (p. 339).

In this way nitro derivatives of anthraquinone are prepared on an industrial scale from corresponding derivatives of aminoanthraquinonc (Kopetsehni [212]; Mosby and Berry [213]). This is rather advantageous since pure individuals are obtained instead of the mixtures of isomers which would be formed if anthraquinone were nitrated.

Aminopyridines are especially convenient as a starting material for the preparation of nitropyridines by oxidizing the amino group. Kirpal and Böhm [214] have obtained 2-nitro- and 4-nitro-pyridines by this method.

Among other oxidizing agents which can be used for the conversion of the amino group to the nitroso and nitro group the following compounds should be mentioned: peracetic acid (D'Ans and Kneip [215], Greenspan [216], Mosby and Berry [213]), an aqueous solution of sodium peroxide (O. Fischer, Trost [217]), and an acid solution of ammonium persulphate with addition of silver nitrate as a catalyst (Witt and Kopetschni [218]).

Emmons [177] has recently suggested the oxidation of anilines to nitrobenzenes by trifluoroperacetic acid (CF_3.COOOH). He obtained high yields, for example:

TABLE 14

Substrate	Product
Aniline	89% of nitrobenzene
o- Nitroaniline	92% of *o*- dinitrobenzene
p- Nitroaniline	94% of *p*- dinitrobenzene
p- Phenylenediamine	86% of *p*- dinitrobenzene
p- Toluidine	78% of *p*- nitrotoluene
2,4-Dinitroaniline	87% of 1,2,4-trinitrobcnzene

2,4,6-Tribromo- and -trichloro-aniline give nearly theoretical yields of 2,4,6-tribromo- and -trichloro- 1- nitrobenzene (100% and 98% respectively).

The method of conversion of an amino into a nitro group has not found application in the nitration of aliphatic amines, since only insignificant yields of nitroso and nitro compounds could have been obtained together with considerable quantities of oxidation products. For example, ethylamine, reacted with Caro's acid, yields, according to Bamberger [219], the following products: acetic acid, as the principal product and along will1 it small quantities of nitroethane, acetohydroxamic acid, acetoxime and acetonitrile. If an amino group is attached to a tertiary alkyl carbon, higher yields of nitroso compounds can be obtained. Thus, tert-butylamine gives oxime in good yield, and then nitroso-tert-butane is obtained (Bamberger and Tschirner [220]).

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CHAPTER IV

NITRATION WITH NITRATING MIXTURES

NITRATING MIXTURES

COMPOSITION OF NITRATING MIXTURES

THE composition of a nitrating mixture should be chosen very carefully with regard to the compound being nitrated and the number of nitro groups to be introduced. It is clear that the more nitro groups to be introduced, the higher the acid concentration should be.

The nitration of aromatic compounds is carried out with only a slight excess of nitric acid. This is smaller when lower nitrated compounds are prepared (0.2-5% of HNO_3 in excess of the calculated weight) and larger when higher nitrated compounds are to be obtained (3-100% or more in excess of the calculated weight of HNO_3).

The ratio of the quantities of components of the nitrating acid, HNO_3, H_2SO_4 and H_2O, is also important. The fact that water is formed during the nitration process, thus diluting the nitrating mixture, must be taken into consideration. Since among the components of the mixture, sulphuric acid is the principal one which binds water, the amount of H_2SO_4 must be chosen in such a proportion that it can take up all the water formed during the nitration. Otherwise nitration might be incomplete.

The concentration ratio, or the so-called *spent acid strength* or *dehydrating value of sulphuric acid* (D. V. S.) is of importance:

$$\text{D.V.S.} = \frac{[H_2SO_4]}{[H_2O]_i + [H_2O]_f}$$

where: $[H_2O]_i$ is the initial concentration of water in the nitrating mixture before nitrating and $[H_2O]_f$ is the concentration of water formed during nitration.

For example, if benzene is being nitrated according to the equation:

$$\underset{\text{mol. weight}}{\begin{matrix} C_6H_6 \\ 78 \end{matrix}} + \underset{}{\begin{matrix} HNO_3 \\ 63 \end{matrix}} \rightarrow \underset{}{\begin{matrix} C_6H_5NO_2 \\ 123 \end{matrix}} + \underset{}{\begin{matrix} H_2O \\ 18 \end{matrix}} \qquad (1)$$

with a mixture:

HNO_3	32%
H_2SO_4	60%
H_2O	8%

then for each 100 kg of mixed acids, i.e. for 32 kg of HNO_3, x kg of water is formed.

$$x = \frac{18 \times 32}{63} = 9.14 \text{ kg} = [H_2O]_f$$

hence

$$\text{D.V.S.} = \frac{60}{8 + 9.14} = 3.50$$

This is the "theoretical" value of D.V.S. In practical work allowance should be made for the presence of the excess of HNO_3 used. The above calculations may be made with theoretical reference to either hydrocarbon or nitric acid. When 95% of the theoretical hydrocarbon is used, the hydrocarbon factor is calculated. :

$$\frac{C_6H_6}{HNO_3} = \frac{78}{63} = 1.24$$

Hydrocarbon factor = 1.24 x 95% = 1.18

Water of nitration per 100 kg of hydrocarbon is $= \frac{18 \times 100}{78} = 23.08$

HNO_3 used in the mixed acid is:

1.18*32 = 37.76 kg HNO_3 per 100 kg of mixed acid.

Hence the water of nitration per 100 kg of mixed acid = $\frac{37.76 \times 23.08}{100} = 8.71$

$$\text{D.V.S.} = \frac{60}{8 + 8.71} = 3.59$$

Instead of 95% of hydrocarbon, 105% of nitric acid can be used:

$$\frac{HNO_3}{C_6H_6} = \frac{63}{78} = 0.808$$

Nitric acid factor = 0.808 x 105% = 0.848.
HNO_3 used in mixed acid is:

$$\frac{32}{0.848} = 37.74 \text{ kg } HNO_3 \text{ per 100 kg of mixed acid.}$$

This gives approximately the same figure for the water of nitration per 100 kg of mixed acid :

$$\frac{37.74 \times 23.08}{100} 8.71 \text{ and D.V.S.} = 3.59$$

(according to Groggins [1]).

The D.V.S. should be as high as possible. For example if benzene is nitrated with two acid mixtures A and B, both containing the same quantity of water but having different D.V.S. values, nitration with the A mixture, for which D.V.S.

= 2.96, is incomplete, while with the B mixture, where D.V.S. = 3.5, results in complete nitration. The mixtures have the following composition:

A HNO_3 38.0%, H_2SO_4 54.0%, H_2O 8.0%
B HNO_3 32.0%, H_2SO_4 60.0%, H_2O 8.0%

The nitrating acid and its weight should also be carefully chosen so as to obtain a spent acid with a composition corresponding, where possible, to the lowest solubility of the nitration product in it.

In the U.S.S.R., the D.V.S. is often named the *coefficient of dehydration and* a slightly different way of calculating the nitric composition of sulphuric acid mixtures is in use there. This is *F* or "f.n.a.", the *factor of nitrating activity* suggested by Kholevo. According to Gorst [2], it is the concentration of sulphuric acid in the mixture when the nitric acid is converted into the equivalent quantity of water.

Here is the method of calculating *F* according to the same author.

Let the symbols S, ***N, S'*** denote the following:

S - % concentration of H_2SO_4 in the mixture

N - % concentration of HNO_3 in the mixture used for nitration

S' - % concentration of H_2SO_4 in the spent acid, when all the nitric acid ***N*** is used and from 1 mol. of HNO_3 1 mol. of H_2O is formed.

One kg of HNO_3 yields z = 0.286 kg of H_2O.

The weight of the nitrating mixture is therefore reduced by l-0.286 = 0.714 kg for every kg of HNO_3. The reduction of the weight of 100 kg is 0.714 N.

The concentration of H_2SO_4 in the spent acid ***S'*** will be:

$$S' = \frac{100\ S}{100-0.714\ N}$$

or

$$S' = \frac{140\ S}{140-N}$$

The expression for is:

$$\Phi = \frac{140\ S}{140-N}$$

or

$$\Phi = \frac{S}{1-\frac{N}{140}}$$

It is not advisable to use a high value of the factor of nitrating activity *F* for economic reasons. Nor should low *F*, be applied as this leads to incomplete utilization of the nitric acid in the nitrating mixture.

Orlova [3] gives a number of examples of the values of *F* and of the quantity of HNO_3 used during the nitration (Table 15).

When F (the quantity of sulphuric acid in the spent acid) is given, it is easy to calculate the quantity of sulphuric acid to be used.

If G_N is the quantity (in kg) of nitric acid of concentration N (% HNO_3) and G_s is the quantity (in kg) of sulphuric acid of concentration S (% HNO_3), the quantity of the spent acid can be expressed as:

$$G_S + G_N \frac{100-0.714\ N}{100}$$

TABLE 15

Nitration	F	Quantity of HNO_3 in % of theory
Benzene to NB	70	103-105
NB to DNB	88	110-115
Toluene to MNT	70	103-105
MNT to DNT	82	110-115
DNT to TNT:		
in the three stage process	93	180-200
in the two stage process	87	170-l 80
Xylene to DNX	72	110-115
DNX to TNX	90	150-160
Naphthalene to MNN	61	103-105
MNN to DNN	72	130-140

Notation: NB - nitrobenzene., DNB - dinitrobenzene, MNT - mononitrotolueoe. DNT - dinitrotoluene, TNT - trinitrotoluene, DNX - dinitroxylene, TNX - trinitroxylene, MNN - monottitronaphthalene, DNN - dinitronaphthaleoe.

The quantity of sulphuric acid in the spent acid in per cent F can be calculated as a ratio between the quantity of H_2SO_4 used for nitration $G_S \frac{S}{100}$ and the quantity of spent acid:

$$\Phi = \frac{G_S \times S \times 100}{100\ G_S + G_N(100-0.714\ N)}\ \%$$

hence

$$G_S = \frac{G_N}{140} \cdot \frac{140-N}{S-\Phi}$$

(according to Orlova [3]).

UTILIZATION OF SPENT ACID

The spent acid from a nitration process is usually re-used in the process, viz. after being suitably fortsed it is passed from a higher nitration stage to a lower one. For example, spent acid from the manufacture of trinitrotoluene is used for the

nitration of mononitro- to dinitro-toluene while the spent acid from the latter is used for the nitration of toluene to mononitrotoluene. The portion of the spent acid re-used is sometimes called re-cycle acid.

There are two ways of utilizing the spent acid in the nitration process:

(1) An earlier method, which consists in blending the spent acid with concentrated nitric acid and oleum in such proportion as to obtain a mixture of the exact composition required for the manufacture of the nitro compound to be produced. A drawback of this method is that the compound being nitrated is mixed with concentrated acid. Therefore the nitration may sometimes proceed too vigorously. Taking this into consideration, the reaction must be very carefully controlled, avoiding any rise of temperature, especially in the initial period of nitration.

The rise of temperature is brought about not only by the heat generated by the reaction, but also by the heat of dilution of the nitrating acid by the water formed during the nitration.

The more concentrated the acid, the higher the heat of dilution (Table 16). Therefore, the temperature jump caused by the formation of a given amount of water is higher in the initial period of nitration than at a later stage after dilution has taken place.

Heat capacity also affects the rise of temperature during nitration. Since the heat capacity of a concentrated acid is much lower than that of a dilute acid (Table 17), the same amount of heat generated brings about a higher rise of temperature at the beginning of the nitration than at the end. So this is yet another factor which makes for difficulties when carrying out nitration with concentrated acid.

The considerable effect of accumulated heat and a big rise of temperature may be avoided by applying a more modern method such as that described below.

(2) The substance to be nitrated is mixed with the spent acid and then nitric acid is introduced slowly, the concentration of the acid being increased gradually so that nitration proceeds slowly.

As soon as the substance being nitrated is mixed with the spent acid, it uses up the HNO_3 present in it. Further addition of nitric and sulphuric acids does not result in such a considerable rise of temperature as that occurring in the first method. Two reasons account for this:

(a) The water formed during the nitration process, when evolved in the already dilute acid, does not produce such a large quantity of heat as in the first method (heat of dilution of sulphuric and nitric acids and their mixtures are given in Table 16 (Rhodes and Nelson's data [4]). See also [16].

(b) As mentioned above the heat capacity of dilute acid is higher than that of concentrated acid. For this reason, during the initial period of the reaction when the acid is more dilute the rise of temperature is lower than when, on adding concentrated nitric and sulphuric acids or oleum, an increase in concentration takes place.

It follows from the above that nitration by the second method is safer. It may

TABLE 16

HEAT OF DILUTION OF NITRATING ACID

Ratio $\frac{H_2SO_4}{HNO_3}$		Ratio $\frac{H_2O}{acid}$		Total heat of dilution by adding 500 moles of H_2O	
mole	weight	mole	weight %	kcal/mole	kcal/kg
100	100	0.0	0.0	18.26	84.4
0	0	0.5	8.42	14.53	61.5
		1.0	15.5	11.57	45.1
		1.5	21.6	9.47	34.3
		2.0	26.9	8.28	28.0
		3.0	35.5	6.56	19.7
85.3	90	0.016	0.3	15.10	73.6
14.7	10	0.435	7.78	12.83	57.7
		0.943	15.47	10.19	42.1
		1.56	23.22	8.06	30.2
		3.41	39.8	5.08	14.9
68.5	78	'0.015	0.3	13.23	68.5
30.5	22	0.277	5.4	11.70	57.5
		0.631	11.5	10.15	46.1
		1.282	20.9	7.65	31.5
		2.14	30.6	5.78	20.9
		3.485	41.8	4.10	12.3
54.7	65.3	0.014	0.3	11.67	64.3
45.3	34.7	0.418	8.4	9.66	48.9
		0.818	15.2	8.34	39.1
		1.47	24.4	6.14	25.7
		2.91	38.9	3.95	15.4
39.2	50	0.013	0.3	10.13	59.9
60.8	50	0.27	5.97	8.90	49.4
		1.008	19.15	6.16	29.5
		1.93	31.2	4.35	17.6
		3.03	41.6	3.03	10.3
0	0	0.0	0.0	7.43	53.4
100	100	1.0	22.2	4.16	23.2
		2.0	36.4	2.65	12.1
		3.0	46.2	1.72	6.7

be carried out at higher temperatures without any risk of exceeding the safety limit and due to the higher temperature, nitration can proceed more rapidly.

Gelfman [5] has revised the generally accepted data for calculation of the heat generated during mixing the acids and during their dilution with water [16]. He found the absolute value of the heat generated in the reaction between sulphuric and nitric acids to be lower in the presence of water than when the acids are in an anhydrous state. He also found it decreased on diluting the acids with water. This relationship presented graphically is close to a linear one (Fig. 19). On the diagram

TABLE 17

PHYSICAL PROPERTIES OF SULPHURIC ACID

Specific gravity	H_2SO_4 %	Specific heat cal/g
1.84	98.5	0.33
1.82	90.0	0.36
1.77	83.4	0.38
1.71	77.5	0.41
1.61	69.0	0.45
1.53	62.5	0.49
1.45	55.0	0.55

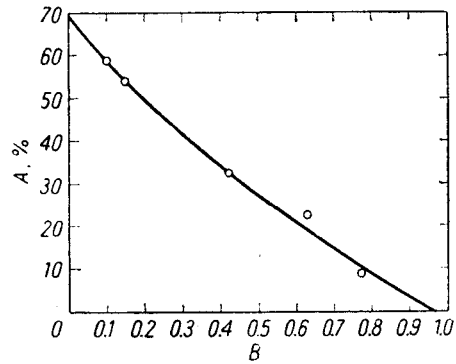

FIG. 19. Heat evolved on mixing nitric acid with sulphuric acid in relation to the water content ***A*** in these acids. Quantity of heat Q = *A B* (Gelfman [5]).

A is the percentage of water in the mixture and ***B*** the coefficient of the thermal effect of mixing the acid, It ranges from 1 (maximum value) for anhydrous acids, and is zero for water. The thermal effect of mixing hydrated acids will be expressed by the product ***B*Q,*** where Q is a value taken from another of Gelfman's diagrams (Fig. 20).

In this diagram the heat of interaction between the anhydrous acids, H_2SO_4, and HNO_3, calculated on 100 g of mixture, has been presented, where Q is the heat of mixing (in calories) and x is the H_2SO_4 content in the mixtures (wt. %). The heat maximum corresponds to x = ca. 67% of H_2SO_4.

Gelfman points out that the heat of interaction between sulphuric and nitric acids is the heat of reaction for:

$$HNO_3 + H_2SO_4 <-> NO_2+ + HSO_4^- + H_2O \quad (2)$$

The interaction heat must not be identified with the heat of mixing. On adding water to The mixture, the equilibrium is shifted to the left. Therefore the heat of

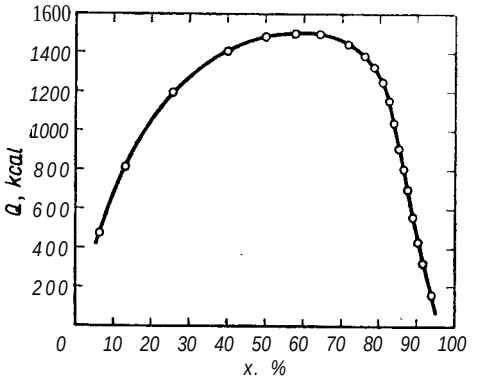

FIG. 20. Dependence of the heat of mixing Q of anhydrous HNO_3 and H_2SO_4 on the content of H_2SO_4 (x %) in the mixture (Gelfman [5]).

interaction between sulphuric and nitric acids in the presence of water is lower than that between anhydrous acids.

During nitration partial separation of the acids takes place. This is the inverse of the mixing process. The absolute value of the thermal effect of separation equals, of course, that of mixing, but its value is negative. For this reason the thermal effects of nitration calculated so far have been too high.

For example, the conversion of phenol into picric acid is accompanied by the generation of 917.4 kcal per kg of the phenol, whereas the thermal effect, calculated by earlier methods, was 1106 kcal/kg.

Similarly the heat of O-nitration of 1000 kg of glycerol with a nitrating mixture comprising 5000 kg of HNO_3 (50%) and H_2SO_4 (50%) is 251,669 kcal, though according to earlier calculations it was 347,000 kcal.

ENTHALPY OF NITRATING MIXTURES

Figure 21 is a diagram by McKinley and Brown [6] showing the relative enthalpies of nitric and sulphuric acids and their mixlures. Another diagram (Fig. 22) shows the relationship between the specific heat of mixtures of acids and their composition.

From diagrams it is possible to calculate the relative enthalpies of nitrating mixtures and of the heats generated during the mixing of acids. The following examples illustrate how to use the diagrams:

Example 1. To find the relative enthalpy of a mixture of acids:

HNO_3	30%
H_2SO_4	20%
H_2O	50%

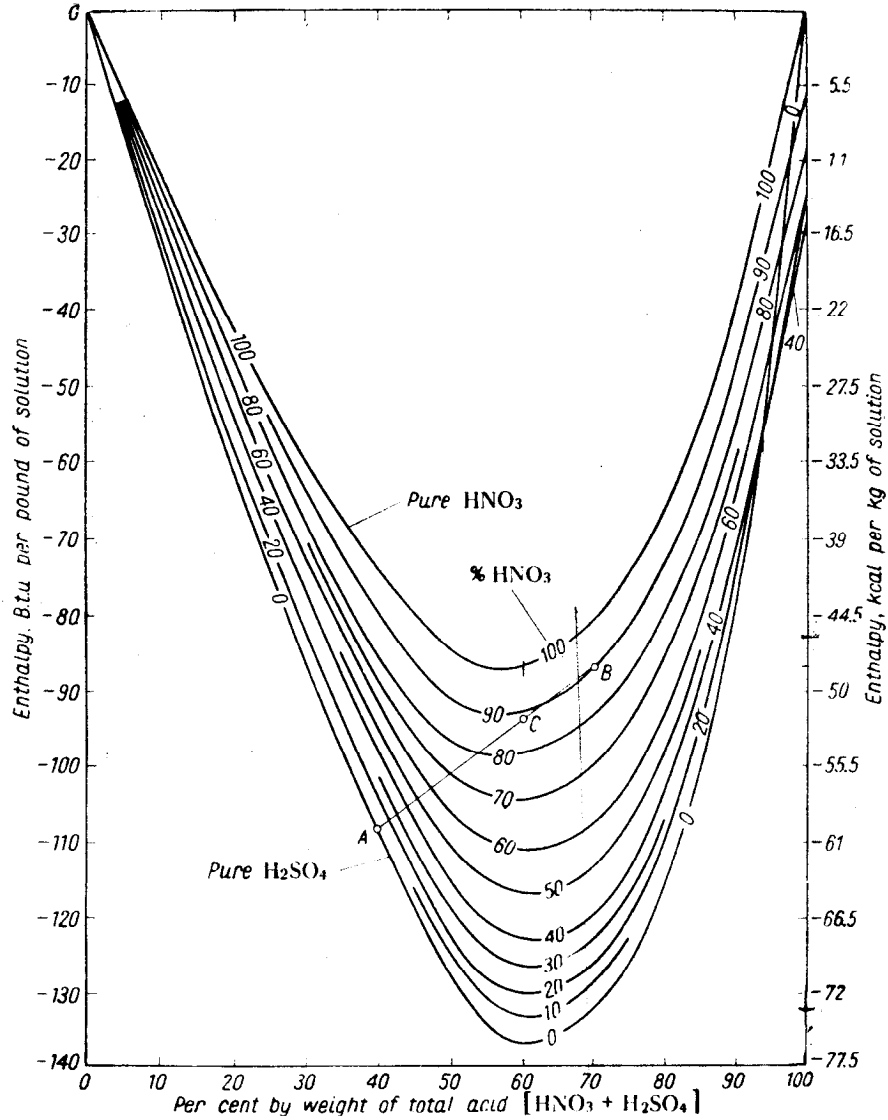

FIG. 21. Enthalpy of nitric acid, sulphuric acid, and water mixtures (McKinley and Brown [6]).

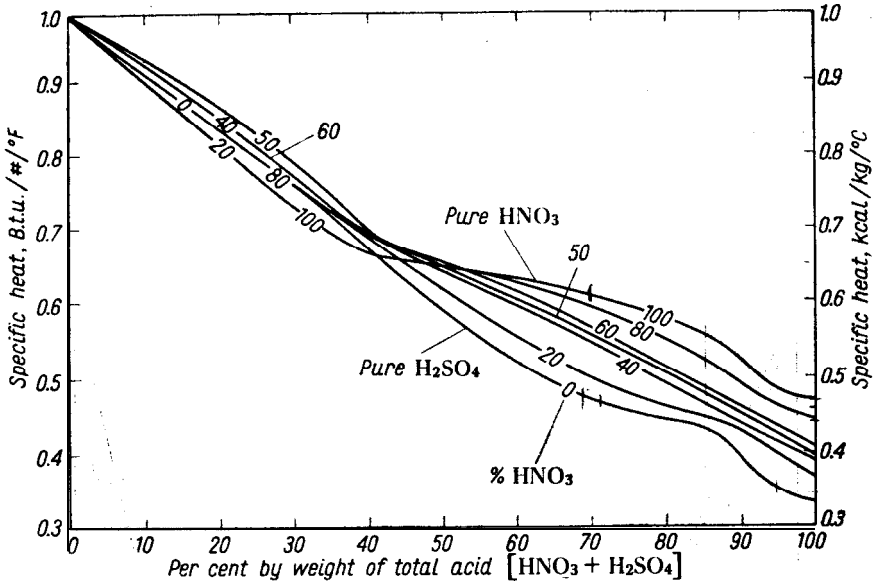

FIG. 22. Specific heat of nitric acid, sulphuric acid, and water mixtures (McKinley and Brown [6]).

at a temperature of 32°C. The total acid content in the mixture is 50%, and the HNO_3 content in the anhydrous mixture is 30/50 x 100 = 60%.

The value 50 corresponding to the total acid in the mixture is found on the x-axis (Fig. 21) and then the point of intersection of the coordinate with the curve, that represents the 60% content of HNO_3 in the mixture of acids, is sought. The ordinate of this point gives the enthalpy value at 0°C equal -58.8 kcal/kg. In the diagram shown in Fig. 22, the specific heat of the mixture is found in an analogous way. It equals 0.66 kcal/kg°C.

Hence the relative enthalpy of the acid at 32°C is:

$$H_{32} = -58.8 + 6.66\ (32\text{-}O) = -\ 37.7\ \text{kcal/kg}$$

Example 2. A mixture of acids having a temperature of 35°C and the composition:

HNO_3	21%
H_2SO_4	62%
H_2O	17%

is to be prepared.

To obtain 100 kg of the mixture, it is necessary to mix:

30.0 kg of 70% nitric acid
65.3 kg of 95% sulphuric acid
4.7 kg of water

The temperature of all the compounds should be 24°C

The relative enthalpy of the mixture of acids is calculated in the same way as in example 1, taking into account that the total acid content (HNO_3+H_2SO_4) is 83% and the HNO_3 content in the anhydrous mixture amounts to 25.3%. The relative enthalpies of the mixture are determined from the tables as in example 1.

TABLE 18

	Specific heat Cal/g	Enthalpy at 0°C kcal/kg	Enthalpy at 24°C kcal/kg	Enthalpy at 35°C kcal/kg
Mixture of acids	0.47	-54.8	-	-. 38.3
Nitric acid	0.61	-44.9	-30.5	-
Sulphuric acid	0.36	-24.4	-15.9	-
Water	1.0	0	+24	-

Thus, for the 100 kg mixture the enthalpies of the components at 24°C are:

nitric acid	-30.5 x 30 = - 915.0 kcal
sulphuric acid	-15.9x65.3 = -1038.3 kcal
water	+24 x 4.7 = + 112.8 kcal

The total enthalpy of the components at 24°C is -1840.5 kcal. The enthalpy of 100 kg of the mixture of acids at 35°C is

$$-38.3 \times 100 = -3830 \text{ kcal}$$

Hence the heat which must be removed during the preparation of 100 kg of the mixture so as to maintain 35°C is

$$3830 - 1840.5 = 1989.5 \text{ kcal or } 19.9 \text{ kcal/kg}$$

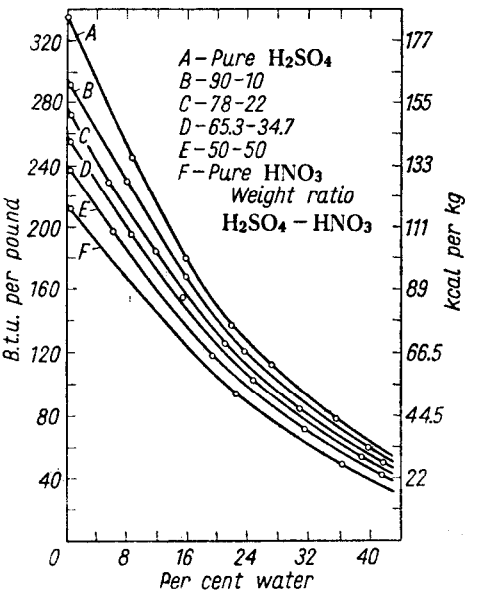

FIG. 23. Heats of dilution of nitric acid, sulphuric acid, and their mixtures (Rhodes and Nelson [4]).

HEATS OF DILUTION

Heats of dilution at 18°C of mixed acid containing various known percentages of sulphuric acid, nitric acid, and water were given in Table 16 (p. 144). The data are presented graphically in Fig. 23. Thus for a mixed acid containing

60% HNO_3 or the weight ratio H_2SO_4/HNO_3 = 40/60 the intercept on the ordinate representing 20% water indicates a heat of dilution of ca. 115 B.t.u. per lb, in agreement with the foregoing calculations. It can be seen from the curves that as the nitration progresses the heats of dilution decrease and as the water content of the nitrating acid increases. There is greater danger of violent or explosive reaction at the early stages of nitration, owing to the 1ower specific heats of the more concentrated acids, than later on in the reaction. (See also [17]).

The curves also indicate why it is comparatively safe to carry out rapid nitration at relatively high temperatures with spent acid or with nitric acid alone.

MIXING THE ACIDS

The operation of mixing is carried out in iron vessels equipped with cooling jackets and stirrer.

A schematic diagram of a mixing plant is given in Fig. 24. It consists of a large vessel (1) for storing the acids, a measuring tank for the acids (2), a mixer (3), a pressure-egg (4) and a vessel for the storage of the prepared nitrating mixture (5):

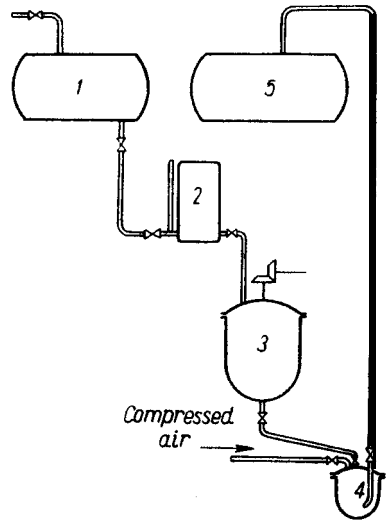

FIG. 24. Diagram of a plant for mixing acids.

Vessels and pipes for concentrated nitric acid are made of pure aluminium. Those for sulphuric acid, oleum and the mixture of acids are made of iron. Steam pipes must be laid close to oleum pipes and the whole should be coated with thermal insulation. In this way the oleum pipes are heated, thus preventing the oleum from freezing in winter.

Calculation of acid mixtures. A mixture of the composition:

HNO_3	A%
H_2SO_4	B%

is to be prepared from:

(1) n% nitric acid
(2) s% sulphuric acid
(3) spent acid with n'% H_2SO_4 content and s'% HNO_3 content.

To obtain 100 kg of the mixture we take

x kg of nitric acid
y kg sulphuric acid
z kg of spent acid

The following three equations with three unknowns must then be worked out:

$$x+y+z = 100$$
$$zn' +xn = A$$
$$zs'+ys = B$$

By solving the system of equations we obtain the formulae for the calcnlation of x, y, r.

$$x = \frac{A(s-s') + n'(B-100s)}{s(n-n')-ns'}$$

$$y = \frac{B(n--n) + s'(A-100n)}{s(n-n')-ns'}$$

$$z = \frac{n(100s - B) - As}{s(n-n')-m'}$$

If oleum is used it is assumed that

$$s = p+1.225\ g$$

where p and g are the percentages of H_2SO_4 and SO_3 in the oleum respectively (122.5 parts of H_2SO_4 are obtained from 100 parts of SO_3).

TEMPERATURE OF NITRATION

The nitration temperature has considerably less effect on the position of the nitro group in an aromatic nucleus than for example the sulphonation temperature. Nevertheless, keeping the desired temperature constant is of greatest importance from the viewpoint of safety and of the purity of the product. The use of too high a temperature causes the reaction to proceed violently. At high temperature by-products, especially oxidation products, are readily formed. The oxidation reactions are accompanied by the evolution of nitrogen dioxide. This is why the temperature must be kept as low as possible, especially at the initial stage of reaction when the substance is not yet or only at the initial stage of the nitration.

The safety limit of temperature depends on the chemical structure of the compound being nitrated. For example, in the nitration of dinitrotoluene to trinitrotoluene or of phenol to picric acid, temperatures near 120°C and over are considered dangerous. In the nitration of dimethylaniline to tetryl, a temperature higher than 80°C must be considered dangerous. Esterification with nitric acid should be carried out at a temperature close to room temperature or lower.

MIXING OF REAGENTS DURING NITRATION

There are three methods of mixing organic substances to be nitrated with nitrating mixtures:

(1) adding the substance to the acid,
(2) adding the acid to the substance,
(3) simultaneous introduction of both acid and organic substance into the nitrator.

The first method is the one most frequently applied. It has, however, certain drawbacks. The first portions of the nitrated substance are introduced into an excess of nitrating mixture and may be converted to a higher degree of nitration than required and may also undergo oxidation processes; hence the uniformity of the product may not be satisfactory. Also some substances sensitive to concentrated acid may be decomposed by contact with an excess of acid necessitating application of the second method. In the second method the substance to be nitrated is contacted with an inadequate quantity of nitrating acid. This might be advantageous for the reason mentioned above. However, when aromatic hydrocarbons with alkyl side groups (e.g. toluene) are nitrated, reaction of the hydrocarbon with an inadequate amount of nitrating mixture may lead to the formation of dark coloured complex compounds and even tarry matter (see p. 77). In this instance the first method is more advantageous. The best method, which consists in simultaneous introduction of both reactants into the nitrator, has the advantage that it is applicable in continuous nitration processes.

As already mentioned earlier, nitration proceeds mainly in the acid phase. Strictly speaking the acid phase consists of an acid saturated with an organic substance. On the other hand, the organic phase is in turn saturated with an acid. The reaction rate in an acid phase is much higher than that in an organic phase (see p. 40). By vigorous stirring the contents of the nitrator are kept emulsified and the phases are kept mutually saturated due to diffusion over a very large interfacial area.

Insufficient mixing may easily result in a low nitration rate owing to the small interfacial area. It can also lead to a non-uniform nitration process. Owing to inadequate construction of the stirrer, too low a speed of rotation, or an interruption in stirring, so-called dead spaces may easily be formed in which non nitrated or not fully nitrated substances accumulate. If a rather large quantity of the mixture is stirred suddenly, rapid extension of the interfacial area takes place, followed by the generation of large amounts of heat and a rise in temperature. This may cause a spontaneous decomposition of the reaction mass in the nitrator, and then an explosion.

Such an accident, well known in the history of the chemical industry, happened at the Rummelsburg factory in 1914 during the nitration of benzene. The transmission belt slipped off and caused the stirrer to stop. In spite of this benzene continued to flow into the nitrator. When the fault was noticed, the stirrer

was set in motion by putting the belt in the right place, with the result that an explosion followed (see also p. 446).

Stirring should be particularly vigorous at the beginning of nitration when the reaction is most violent and the largest amount of heat is evolved. There is a further reason which makes very fast stirring necessary at the beginning, namely the fact that the two liquid phases-that of a light substance being nitrated and that of the heavy nitrating acid-differ considerably in specific weight. As the reaction goes on, and the organic phase is nitrated, its specific weight increases while that of the acid decreases because of its dilution. Toward the end of nitration, the difference between specific weights having been much reduced, mixing of the two phases is greatly facilitated.

A few workers have investigated recently the problem of the influence of stirring on the rate of nitration and the yield of the reaction. McKinly and White [7] reported that the rate of nitration of toluene to nitrotoluene increased by 3% only when the stirring speed was increased from 1327 to 2004 r.p.m.

However, much larger increases (4 to 5 times higher) were obtained in the same reaction by Barduhn and Kobe [8] when they changed the stirring rate from 1000 to 2175 r.p.m.

The results of their experiments are given in Fig. 25.

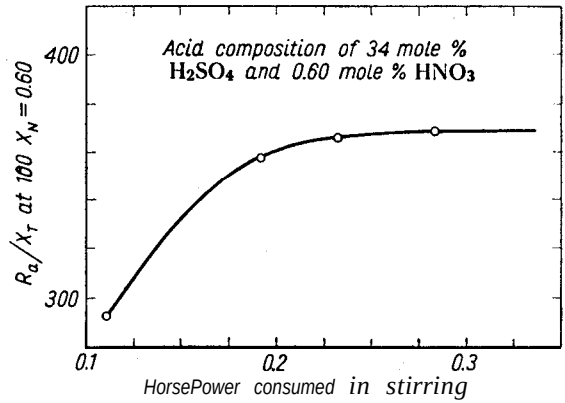

FIG. 25. Rate of nitration (R_a) as a function of stirring rate: X_T and X_N are the concentrations of toluene and nitric acid respectively. (Barduhn and Kobe [8]).

SOLUBILITY OF NITRO COMPOUNDS

The solubility of a substance being nitrated in the acid used is an important factor in the nitration process. The more easily the substance dissolves in the acid, the higher the reaction rate, and hence the higher degree of nitration to be obtained during a given time.

Since aromatic compounds are more ready soluble in sulphuric acid and in mixtures in which its concentration is high, completion of full nitration is accelerated by using such mixtures. The solubility of dinitrobenzene in sulphuric acid of various concentrations and at various temperatures is shown in Fig. 26.

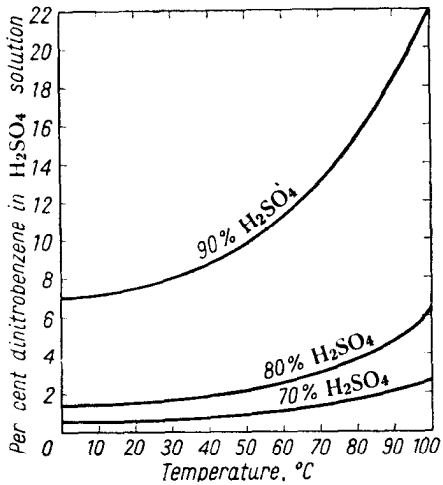

FIG. 26. Solubility of *m*- dinitrobenzene in sulphuric acid (Groggins *et al.* [1]).

Sometimes it is difficult to fulfill all the conditions a nitration mixture should satisfy, such as a low solubility of the nitro compound at an adequate strength of the acid. Sometimes water may be added, after the nitration has been completed, to reduce the solubility of the nitro compound so as to obtain quantitative separation of the product. This can be justified economically although the acid becomes diluted, thus necessitating the use of more oleum for fortifying the spent acid.

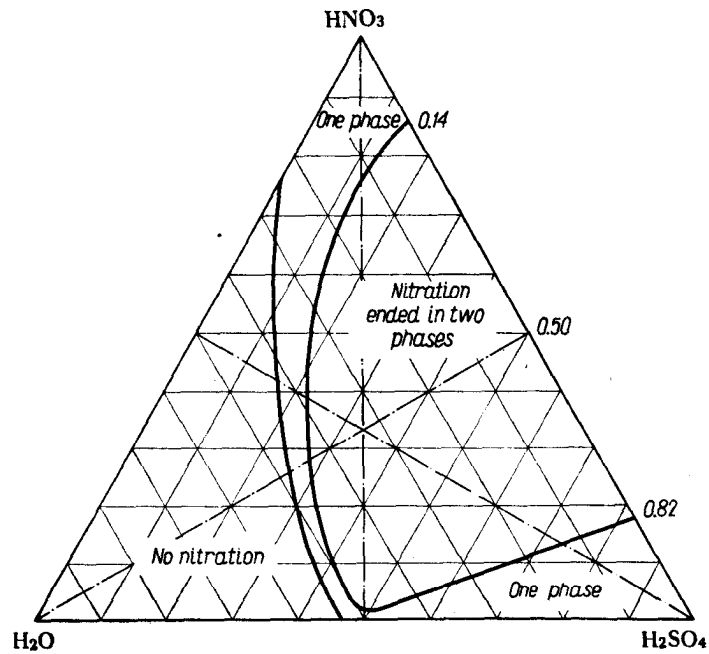

FIG 27. Influence of the concentration of nitrating mixtures on the nitration of nitrobenzene to dinitrobenzene and phase conditions after cooling to 35°C (Hetherington and Masson [9]).

Figure 27 shows the influence of the concentration of a nitrating mixture on the nitration of nitrobenzene and the phase conditions at the completion of the nitration of nitrobenzene to dinitrobenzene, after cooling the mixture down to 35°C. The relationship between the rate of nitration of benzene to dinitrobenzene and the

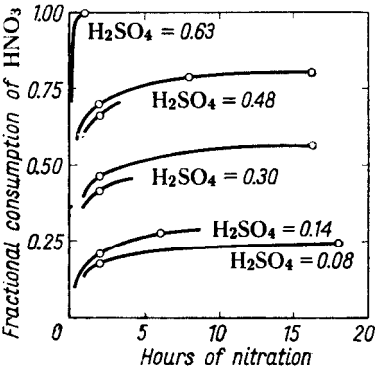

FIG. 28. Rate of nitration of benzene to dinitrobenzene as a function of the molar concentration of sulphuric acid. (Various curves correspond to various molar concentrations of H_2SO_4, when $[HNO_3] = 1$.) (Hetherington and Masson [9]).

molar concentration of sulphuric acid arc shown in Fig. 28 (Hetherington and Masson's data [9]).

The influence of sulphuric acid in O-nitration processes, as for example in the esterification of cellulose with a mixture of sulphuric and nitric acids, appears to be somewhat different. This will be dealt with in the chapter on esters (Vol. II).

DESIGN OF NITRATORS

The nitrators used in the manufacture of aromatic nitro compounds consist of iron vessels (Fig. 29), equipped with a stirrer (I) and a jacket (2) for cooling or heating the contents, as well as with a lid (3), connected with a ventilation pipe (4). Gaseous products from the nitration process (NO, NO_2, HNO_3, SO_3, SO_2, CO, CO_2) are conducted away through it. The ventilation duct is equipped with a sight glass (5), which permits the observation of waste gases - mainly their colour.

In addition to the ventilation duct the lid is equipped with two feed pipes, one for acids, (6), and one for the substance to be nitrated, (7), a thermometer sleeve (8), a delivery pipe for compressed air (9) and a pipe (10), reaching down to the bottom, for discharging the nitrator contents by means of compressed air. It is essential to furnish the lid with a manhole (II). During nitration, the manhole opening is closed by a thin sheet of aluminium, which at the same time plays the role of a safety valve in case the pressure should rise inside the vessel.

The nitrator capacity may vary and may be as large as 15 m^3. Its dimensions depend on the compound to be nitrated and on the method of nitration; for example,

nitrators for continuous nitration are as a rule smaller for a given output. More dangerous reactions are also carried out in nitrators of smaller size.

Cast iron was the material most often used for the construction of nitrators, and forged sheet iron less so. Now stainless sheet steel is generally used. Stainless steel sheet must be welded by modern methods (under a hydrogen atmosphere), since otherwise the seam would be a site relatively easily corroded. Formerly before reliable methods of welding had been developed, metal sheets were riveted to fabri-

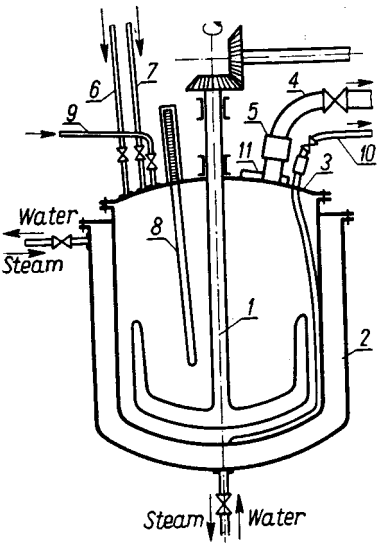

FIG. **29. Diagram of the construction of nitrator.**

cate nitrators. In certain cases sheet lead was widely used, e.g. for the nitration of glycerol. For certain substances easy to nitrate (phenols) earthenware vessels may be used or iron nitrators with an inner lining of an acid resistant ceramic material.

HEAT EXCHANGE DEVICES

If a nitrator is equipped only with a cooling or heating jacket, the ratio of the heat exchange area to the nitrator capacity depends on the latter. When the capacity is cubed the surface area is squared. Thus, when the dimensions of a nitrator are increased, the heat exchange area may no longer be adequate. Then, a stainless steel coil or a lead coil must be mounted inside the nitrator.

STIRRERS

The influence of stirring on the nitration rate and the safety of the operation has already been emphasized. It is evident that special attention must be paid to the stirring equipment provided in a nitrator. Various types of stirrers are used.

Horseshoe stirrers, the shape of which fits well into the inside of a nitrator, are the simplest type (Fig. 29).

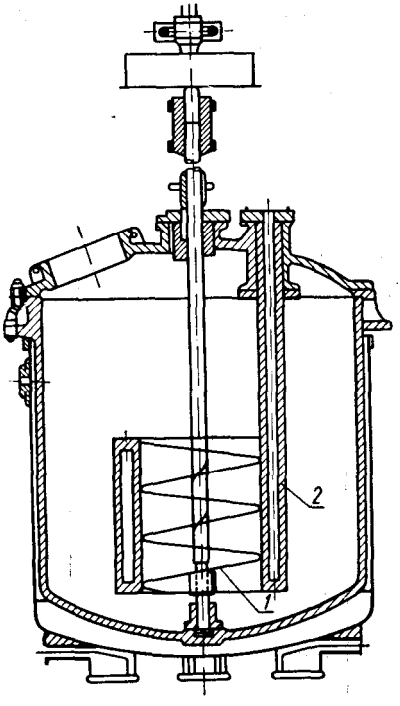

FIG. 30. Diagram of a nitrator with a spiral screw stirrer.

Another type of simple stirrer is one with a set of blades or bars mounted vertically on a vertical axis. A more complex form of this type of stirrer consists of two

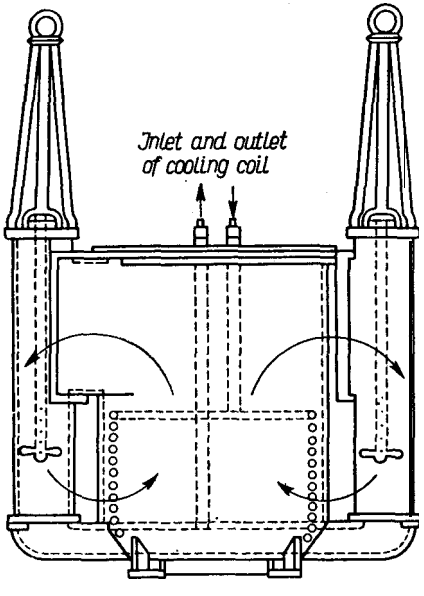

FIG. 31. Diagram of a nitrator with two external chambers.

sets of blades or bars, mounted on two axes, which rotate either in the opposite or in the same direction, sometimes at different speeds. This type of stirrer is used for the nitration of cellulose and is often mounted in small nitrators in which additional internal cooling (or heating) would be difficult to apply.

The types of stirrers mentioned are particularly useful when the contents of the nitrator are highly viscous or semi-liquid, for example a mixture of acid and a crystalline product.

For liquids of low viscosity a spiral screw stirrer may be used (Fig. 30). Circulation can be facilitated by surrounding the stirrer (I) with a sheet metal cylinder

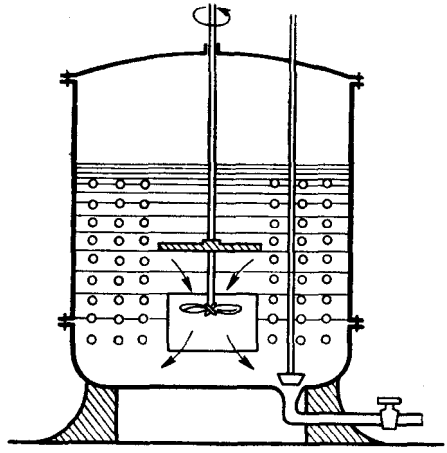

FIG. 32. Diagram of a nitrator with a propeller stirrer.

(2), provided with double walls through which cooling water or steam circulates for additional cooling or heating,

One rather unusual design comprises a mixing system with two external chambers (Fig. 31). The nitrator is connected with both sides of each chamber, in each of which a propeller stirrer is rotated at 200-400 r.p.m. The speed of rotation and cross-sections of the chambers are so selected as to enable the whole of the nitrator contents to make one round within one minute.

Propeller stirrers with the propeller located inside a sheet metal cylinder (Fig. 32) or in the space delineated by a heating coil are frequently used. The propeller draws the liquid from the top of the cylinder, forcing it downwards. In the space between the cylinder and the nitrator walls the liquid flows in the opposite direction. If a well designed propeller is used and a suitable rotation speed applied, circulation of the liquid is sufficient to secure adequate mixing. The system is also used for continuous nitrators, not only for nitration of aromatic compounds, but also for nitration of alcohols, for example glycerol.

Mixing by means of a draw-lift turbine is the most modern and efficient method (Fig. 33). The turbine is rotated at high speed (several hundred r.p.m.) and powered by an electric motor with a worm reduction gear. The turbine draws the liquid

from the top and bottom and throws it out at a tangent. The stream of liquid hits the cooling coil. Then the liquid flows partly upward and partly downward between the coil, some of it being reflected by the coil.

The shape of the nitrator bottom should also be carefully selected for a given stirring system. The efficiency of mixing with a propeller or turbine is higher when the nitrator has a conical or spherical bottom.

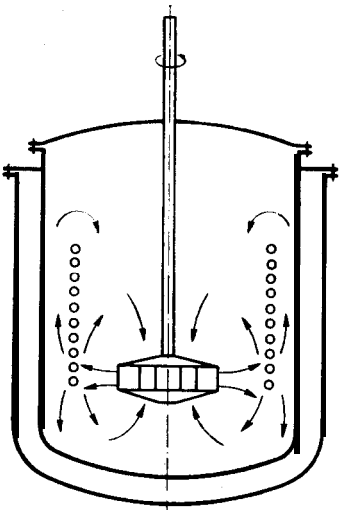

FIG. 33. Diagram of a nitrator with a draw-lift turbine and a cooling coil (circulation of the liquid content is marked with arrows).

The construction of nitrators for the continuous production of nitro compounds is somewhat different. Figure 90 (p. 374) shows a schematic diagram of one type of continuous nitrator. Nitrators for preparing nitric esters (e.g. nitroglycerine, nitrocellulose) are of yet another design. New types of nitrators based on the principle of passing two streams of reacting liquids (organic substance and nitrating acid) through an injector, are now being introduced (Vol. II). They may bring about a radical change in many existing designs of nitration plant.

PRODUCT SEPARATION AND DISCHARGE OF THE NITRATOR

When the reaction has been completed the nitrator contents must remain at rest for some time to allow the product to separate from the spent acid. This may be done in the nitrator itself or the mixture may be transferred into a special settler-separator. The latter is more advantageous if the next nitration is to be carried out in the nitrator immediately after the first reaction.

The nitrator is discharged either through an outlet located in the bottom (Fig. 34) or by forcing the contents out by means of compressed air (Fig. 35). In the latter case the nitrator lid should fit tightly and the fume outlet should also close tightly with a valve. If the nitrator itself has been used as a separator, the spent

acid layer is transferred to a special tank while that of the product goes to another tank (for example direct for washing if it is an end product, or to another nitrator if it is to be nitrated further). To make practicable the transport of the two layers to different locations the discharge pipe should be equipped with a sight glass, through which the partition boundary of the phases can be seen.

An advantage of discharge by means of compressed air is that the whole plant can be located in a low building. If the nitrator is emptied through an outlet in its base a high building is necessary. This is of particular importance when underground plant is to be constructed, for the cost rises considerably as the depth in-

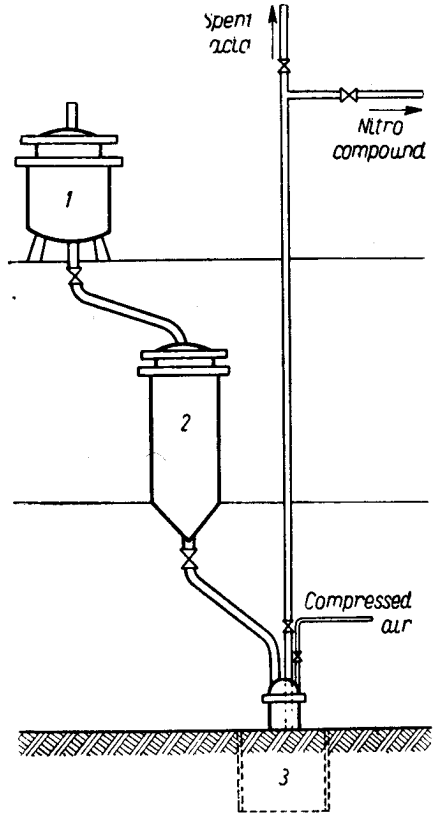

FIG. 34. Flow diagram, nitration, the discharge of the nitrator through the bottom: 1 - nitrator; 2 - separator; 3 - pressure-egg.

creases. A drawback associated with the use of compressed air for discharging the nitrator contents is the risk of damage and the operatives being burned consequent on breakage of the sight glass.

Discharging the nitrator through an outlet has the further drawback that it makes the reactor more difficult to construct.

In the case of substances that solidify (for example, TNT) all pipes and valves should be provided with heating jackets. If the nitration product solidifies at a

high temperature and cannot be kept molten it is necessary to create the necessary conditions to ensure the formation of a fine-crystalline or granular product. It is only then that bottom discharge will be feasible. The nitrator contents are then transported immediately to a centrifuge, or in the case of explosives sensitive to impact (sensitivity of the order of that of tetryl or higher), the solid product is filtered off under reduced pressure.

The separated solid or liquid product is then washed with water in order to remove acids, and subsequently purified according to its properties and the nature of the impurities present. Finally the pure product is obtained in the required physical form.

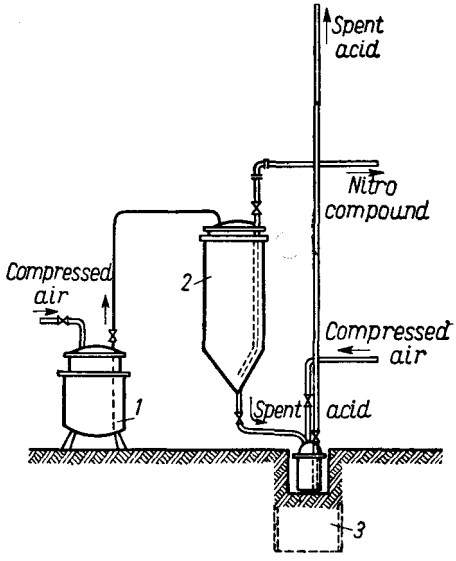

FIG. 35. Flow diagram, nitration discharge of the nitrator by means of the compressed air: 1 - nitrator; 2 - separator; 3 - pressure-egg.

WASTE WATER

The technology of nitration processes is unavoidably associated with the problem of waste water disposal. The water, which comes from washing the nitration product, contains acid components from the nitrating mixture, and nitro compounds.

Both the acids and the nitro compounds in solution, or suspended, or in both states are highly noxious for the flora and fauna of rivers and lakes.

Thus, nitro compounds in a concentration as low as a few milligrams per litre are lethal to fish. Wastes from the manufacture of hexyl (hexanitrodiphenylamine) are particularly toxic, killing fish at a concentration as low as 0.1 mg of hexyl per litre. For this reason, the removal of these compounds from the waste water prior to its discharge is of primary importance.

As a rule acids are removed from waste water by discharging it into pits filled with limestone, where they are neutralized.

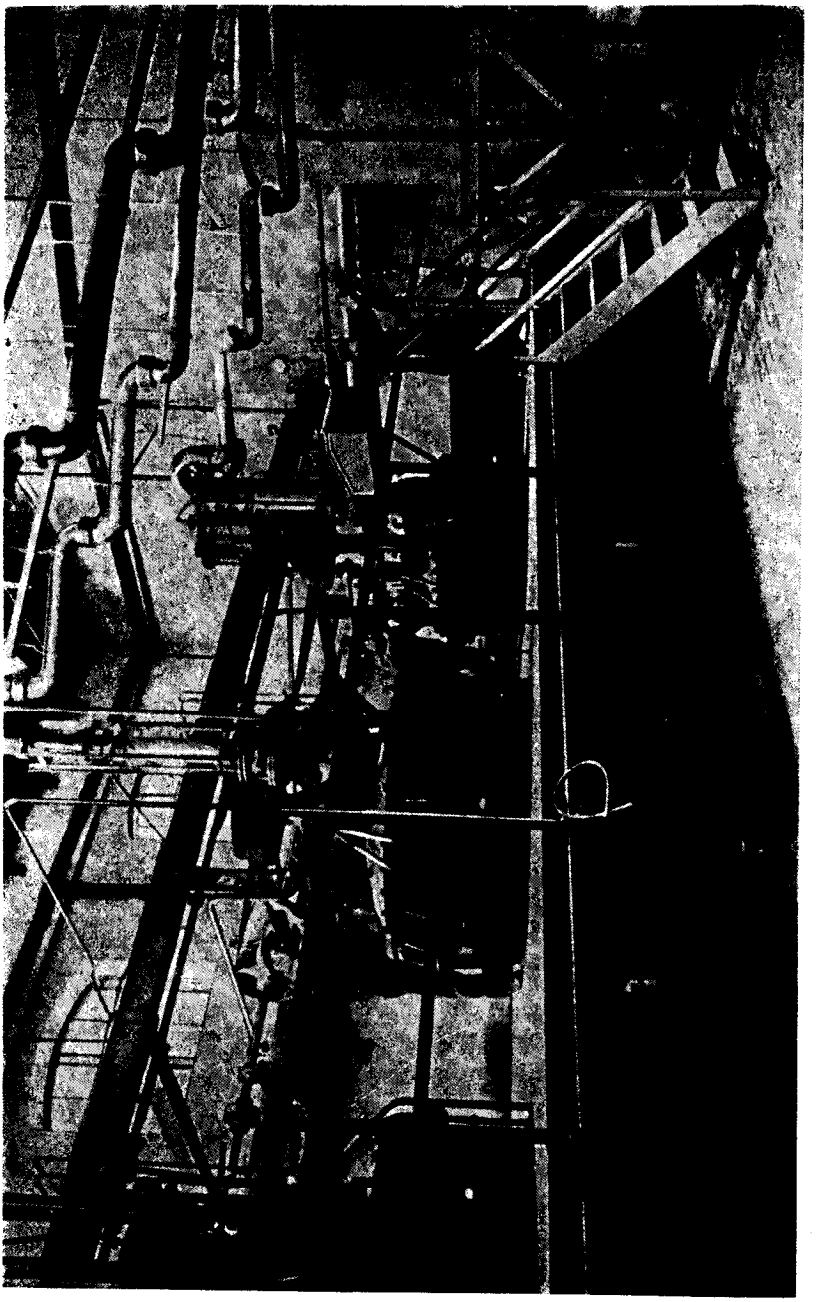

FIG. 36. General view of a nitration room (Bofors Nobelkrut).

Clearly, nitro compounds suspended in water are easily removed by passage through settling tanks or filters. Nitro compounds dissolved in water are most difficult to remove. Various methods are possible, which make use of various physical and chemical properties of the nitro compounds. For example, physical methods which have been suggested and applied include adsorption of the nitro compounds on absorptive agents (e.g. carbon) and extraction with solvents of low volatility (e.g. phthalic esters). Among chemical methods, the destruction of nitro compounds by oxidation with hypochlorous acid is possible. Since nitro compounds are often resistant to oxidation, a more complex process is sometimes more efficient, consisting first of the reduction of the nitro compound, then its oxidation. Chemical methods are generally expensive and are rarely used. In particular, oxidation by hypochlorous acid consumes considerable quantities of chlorine - up to 3 g for 1l of solution.

Biological methods of destroying nitro compounds are of considerable interest. Up to now they have not been practiced on a large scale, but they are promising because of their economy. The first investigations into the possibility of destroying nitro compounds by biological methods were carried out in 1941 by Erikson [10], who found that nitro compounds such as nitrobenzene, picric acid, and trinitroresorcinol can be used as a nutrient by some *Actinomyceres*. The observation was later confirmed by Moore [11] and by Rogovskaya [12], who suggested destroying nitro compounds by fermentation.

Simpson and Evans [I 31 reported that nitrophenols such as o- and p-nitrophenols, 2,4-dinitrophenol or such a nitro compound as chloramphenicol could be destroyed by some ***Pseudomonas*** species to form nitrous acid salts.

According to Petersen [14], the well known herbicide, dinitro-o-cresol, is rapidly deactivated in soil by Gram-positive micro-organisms belonging to the *Corynebacterium* family. This served as a starting point for Jensen and Gundersen [15] in their research work in which they found that *p*- nitrophenol, 2,4-dinitrophenol and picric acid are destroyed by the same micro-organisms with the formation of nitrites. The same authors have investigated the rate of decomposition of dinitro-o-cresol. Moreover, they have observed the interesting fact that *o*- and *m*- nitrophenols, 2,5- and 2,6-dinitrophenols and 3,5-dinitrobenzoic acid do not undergo such a decomposition. It seems that only those nitrophenols that have the nitro group in the *para* position are prone to decomposition.

Since nitro compounds have certain specific properties, which influence the choice of methods for heating wastes, some special methods are described later in the technological section dealing with methods of the manufacture of individual nitro compounds. Diminishing water pollution by washes from the manufacture of TNT is a most complex problem. This will be discussed in detail on p. 390.

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CHAPTER V

GENERAL INFORMATION ON NITRO COMPOUNDS

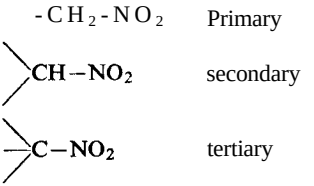
NITRO compounds are substances in which the nitro group is directly attached to a carbon atom:

$$-C-NO_2$$

The evidence for the fact that the nitro group is actually linked with carbon is that reduction of nitro compounds leads to the formation of primary amines

$$-C-NO_2 \rightarrow -C-NH_2 \qquad (1)$$

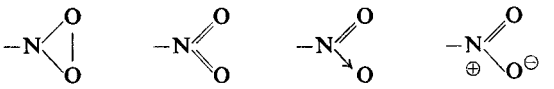
Depending on whether or not and how many hydrogen atoms are linked with a carbon atom, they are known as primary, secondary and tertiary nitro compounds :



All aromatic nitro compounds are tertiary derivatives. Aliphatic or aryl-aliphatic nitro compounds can be primary, secondary and tertiary.

CONSTITUTION OF THE NITRO GROUP

The constitution of the nitro group has been the subject of numerous discussions. Three types of formulae can be found in the literature:



The first of these was abandoned long ago, since the existence of an unstable three-membered ring in such a stable group as the nitro group can hardly be postulated. Besides, the formula does not explain the tautomerism, that exists in primary nitro compounds, analogous to the tautomerism of the CH_2CO system:

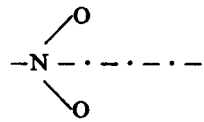
$$-CH_2NO_2 \rightarrow -CH=NO(OH) \quad (2a)$$

$$-CH_2CO- \rightarrow -CH=C(OH)- \quad (2b)$$

Formula II presents a pentacovalent nitrogen atom surrounded by 10 electrons. All five valences are the ordinary, nonpolar ones. Compounds of pentacovalent nitrogen such as the type $N(CH_3)_5$ are not known. On the other hand formulae III present nitrogen as a tetracovalent atom, surrounded by an electron octet. Here, one of the nitrogen atoms is bonded with an oxygen atom by a coordinate (semi-polar) link.

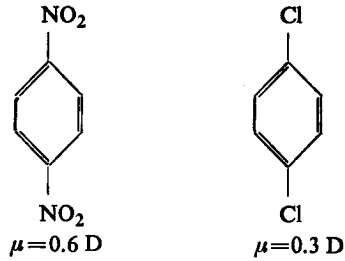
Confirmation of formulae III is provided by data on the molecular refractivity of nitro compounds. The refractivity for the bonds present in formulae III (6.708) is consistent with the experimental data (6.761).

At present formulae III are generally accepted. Nevertheless, they offer some difficulties. Thus, measurements of dipole moments of nitro compounds have shown the nitro group symmetry along the central nitrogen bond:

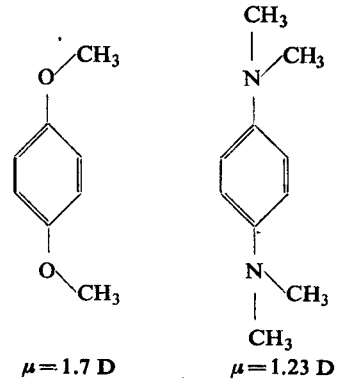


symmetry axis

For example, the dipole moment of p-dinitrobenzene is close to zero, like that of *p*- dichlorobenzene



contrary to, for example, hydroquinone or tetramethyl-p-phenylenediamine esters, which have a relatively high dipole moment, since the substituents introduce asymmetry into molecules:



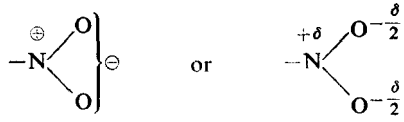
The dipole moment of the nitro group alone, present in an aliphatic nitro compound is :

in the gaseous phase	3.50-3.70 D
in solutions	3.20-3.40 D

In the case of nitrobenzene the dipole moment is:

in the gaseous phase	4.20 D
in solution	4.00 D

For this reason formulae IV are the most probable. They present the negative charge as uniformly distributed between the two oxygen atoms:



IV

The treatment of the nitro group from the molecular orbital point of view is based on the formulae IV. Delocalization of bonds increases its

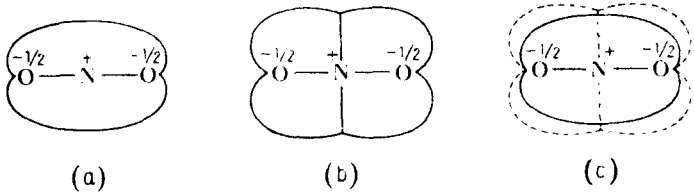
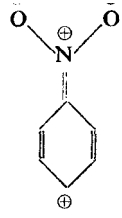


FIG. 37. Molecular orbitals of the nitro group: (a) with the lowest energy level, (b) with the highest energy level, (c) with the ground state energy level [88].

stability - the two oxygen atoms are equivalent. Figure 37 represents: (a) the lowest energy level, (b) the highest energy level and (c) the ground state energy level.

The symmetrical structure of the nitro group is also supported by X-ray analysis of nitro compounds. This is described on the pp. 179- 181.

Likewise, the constitution of, for example, nitrobenzene can be represented as follows:



The formula contains a quinonoid ring to which the slightly yellow colour of nitro compounds can be ascribed. The problem of the quinoid structure of aromatic nitro compounds is discussed on pp. 176, 220.

VISIBLE AND ULTRA-VIOLET ABSORPTION SPECTRA

The nitro group is a chromophor. It produces an absorption band in the ultra-violet region of the spectrum. The position and the intensity of the band depend on several factors which will be discussed later.

In the case of simplest nitro compounds the absorption band produced by this group corresponds to the following values. For aliphatic nitro compounds, for example nitromethane, nitroethane, 1- and 2-nitropropanes, they are: 260-270 mμ at extinctions ε = 40-120. (According to Ungnade and Smiley [l] the values for higher nitroparaffins are 274-278 mμ, ε = 24-41.) For aromatic nitro compounds, such as nitrobenzene the bands are: 250-260 mμ at extinctions ε = 9000-10,000. When a primary or secondary nitro group takes an aci-form, the maximum disappears, as shown by earlier research work of Hantzsch and Voigt [2].

The absorption maximum of a nitro group can be shifted and its intensity may change under the influence of a larger number of nitro groups on the aromatic nucleus.

Changes occurring on the conversion of nitrobenzene to trinitrobenzene have been the subject of investigations of a number of authors (Radulescu and Elexa [3], Kortüm [4], Fielding and Le Févre [5]). All of them obtained similar results. Fielding and Le Févre give the following data for compounds in an alcoholic solution (Table 19).

TABLE 19

Substance	λ_{max} mμ	ε_{max}
Nitrobenzene	260	8130
m- Dinitrobenzene	235	17,400
sym-Trinitrobenzene	225	25,700
Trinitromesitylene	below 220	over 15,800

The data for trinitromesitylene illustrate the steric influence due to the accumulation of substituents around the benzene ring.

Steric influence on the absorption spectra of aromatic nitro compounds has been studied in detail by Brown and Reagan [6]. They investigated the influence of alkyl groups on the absorption spectra curves. As may be seen from the curves, substitution with an alkyl group in the orrho position results in a decrease of the intensity of the nitro group band (compare the absorption spectrum of nitrobenzene with those of *o*- nitrotoluene, *o*- nitrocumene, *o*- nitro-tert-butylbenzene). The larger the alkyl group the stronger its influence. Thus, the band of the nitro group present in *o*- nitro-tert-butylbenzene disappears entirely. The presence of three methyl groups in a molecule gives a similar effect, as may be seen from the nitromesitylene spectrum (Fig. 38).

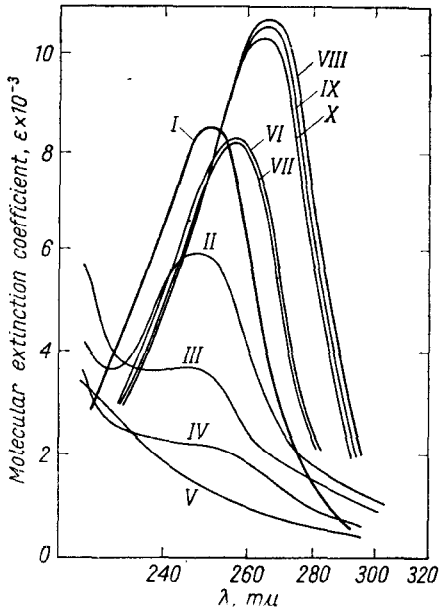


FIG. 38. Absorption spectra of nitrobenzene and its alkyl derivatives: Z-nitrobenzene, II-o-nitrotoluene, III-o-nitrocumene, IV-nitromesitylene, V-o-nitro-tert-butylbenzene, VI-m-nitro-tert-butylbenzene, VII-m-nitrotoluene, VIII-p-nitro-tert-butylbenzene, IX-p-nitrocumene, X-p-nitrotoluene (Brown and Reagan [6]).

A systematic study of the ultra-violet absorption spectra of polynitro compounds were recently carried out by Conduit [7]. By comparing the spectra of isomeric dinitrobenzenes, Conduit came to the conclusion that steric hindrance is responsiblefor the considerable deviation of the spectrum of *o*- dinitrobenzene from those of the two other isomers (Table 20).

He observed a similar effect in isomeric dinitrotoluenes. The most probable

TABLE 20

ULTRA-VIOLET ABSORPTION SPECTRA OF POLYNITRO COMPOUNDS

	λ_{max} mμ	ε_{max}
o- Dinitrobenzene	210	47,600
m- Dinitrobenzene	242	41,300
p- Dinitrobenzene	265	37,140
2,4-Dinitrotoluene	252	39,700
2,6-Dinitrotoluene	241	41,500
1,3,5-Trinitrobenzene	235	42,530
2,4,6-Trinitrotoluene	232	43,100

reason for this is the simultaneous twisting of both o-nitro groups out of plane. Consequently the conjugation of the two nitro groups with the ring is reduced almost to zero.

Methyl groups in nitrotoluenes enhance the conjugation of the nitro groups, except when they are situated in the *ortho* position.

The comparison of the absorption spectrum of *p*- nitrodimethylaniline with those of its derivatives which substituted with the methyl group in the *ortho* position to the nitro group, according to data reported by Remington [8], (see Fig. 39)

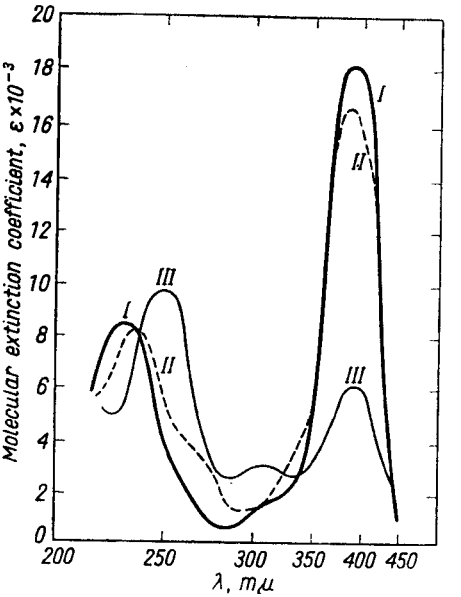
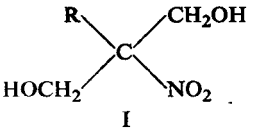


Fig. 39. Absorption spectra of N,N-dimethyl-p-nitroaniline (I) and its methyl derivatives: 3-methyl- (II), 3,5-dimethyl-p-nitrodimethylaniliie (III) (Remington [S]).

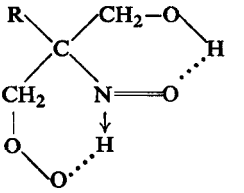
is also of interest. The presence of one methyl group does not have a marked effect upon the absorption spectrum of the nitro group (approx. 260 mμ), but the presence of a second group causes a considerable fall in the intensity of the band. Another band produced by these compounds, near 420 mμ, is less affected by nitro groups.

The influence of aliphatic rings condensed with *p*- nitroaniline or *p*- nitrodimethylaniline has also been studied (Arnold and Richter [9], Arnold and Craig [10]). They decrease the intensity of the nitro group band, and also that of a band near 370-390 mμ.

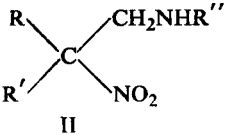
According to T. Urbanski [l l] the band of cu. 270 mμ the nitro group in aliphatic compounds can be considerably weakened or it can even disappear under the influence of hydrogen bonds which link the nitro group with two hydroxyl or one amino group as is shown in schemes Ia and IIa.



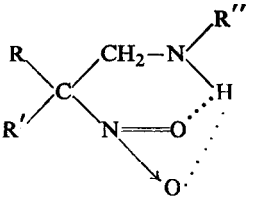
I



Ia (with hydrogen bonds)



II



IIa (with hydrogen bonds)

Consequently the absorption curves of compounds I and II do not contain maxima but only shoulders (Fig. 40). They are shifted towards longer wavelength (bathochromic effect) as compared with the original nitroparaftlns.

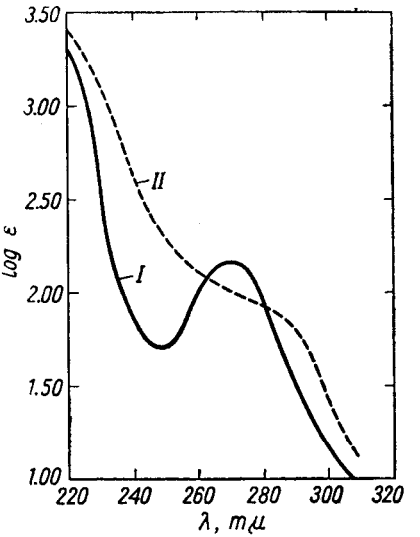


FIG. 40. Absorption spectra of nitroparaffins (I), and nitrodiols and aliphitic aminonitro compounds (II) (T. Urbanski [ll]).

Thus 1-nitropropane shows a maximum at 270 mμ, and the diol (I) obtained from the same compound by adding 2 mol. of formaldehyde shows a bend at 280mμ. A shift of 8-20 mμ was also observed on the corresponding conversion of other nitroparaffins to nitrodiols.

It is important to note that two hydroxyl groups reduce the intensity of the absorption maximum of one nitro group and transform it into a shoulder. One

primary amino group and one secondary amino group can produce the same effect as two nitro groups and one nitro group respectively.

In other words one N-hydrogen atom which is able to form a six-membered ring with one nitro group is sufficient to produce an effect similar to that caused by two hydroxylic hydrogen atoms.

The difference between the ability of a hydroxyl and an amino group to reduce the intensity of the maximum produced by a nitro group may be due to the stronger electron repelling power of amino groups. The much stronger influence of the amino group may serve (according to T. Urbanski) as one of the arguments that the hydrogen bond has mainly an electrostatic character.

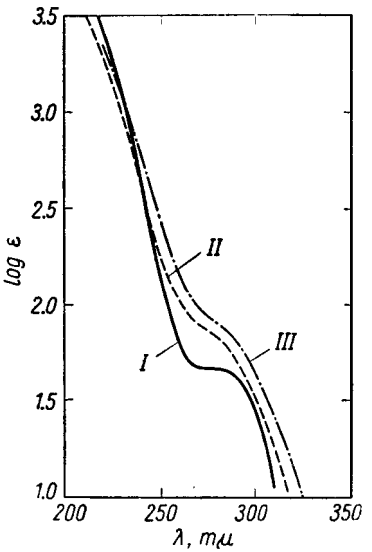


FIG. 41. Absorption spectra of p-halogen derivatives of β– nitroalcohols, e.g. $[(CH_3)_2CHCH_2CH(OH)]_2CXNO_2$: I-X = H, II-X = Cl, III-X = Br (Eckstein, Sobótka and T. Urbanski [12, 13]).

Eckstein, Sobótka and T. Urbanski [12,13] have also found that in β– halogen derivatives of β– nitroalcohols, the shape of the absorption curve depends on the halogen attached to the carbon combined with the nitro group. The increase of the van der Waals radius of the halogen produces a decrease in the intensity of the band characterizing the nitro group. The same rule was observed by the authors when comparing some nitro- and halogenonitro-diols (Fig. 41). This is probably due to the steric effect of shielding the nitro group by a halogen atom.

The influence of a solvent on the absorption spectra of nitro compounds has been examined by several authors. When studying the spectrum of nitromethane, Bayliss and Brackenridge [14] stated that under the influence of a polar solvent the nitro group band underwent a hypsochromic shift (Table 21).

It is interesting to note that ranging from non-polar solvents to sulphuric acid through polar solvents affects aromatic nitro compounds in the opposite direction, i.e. it results in a bathochromic shift. This can be seen from Hammond and Modie's data [15] for nitrobenzene (Table 22).

TABLE 21

ABSORBTION SPECTRA OF NITROMETHANE

Solvent	Absorption maximum mμ
Heptane	277.6
Ethanol	274
Water	268.8
Sulphuric acid	252.5

From the results of investigations into the absorption spectra of nitromethane in non-polar solvents (cyclohexane and carbon tetrachloride) de Maine and his co-workers [16] drew an important conclusion. They found that dilute solutions of nitromethane do not obey Beer's law, unlike more concentrated solutions in

TABLE 22

ABSORPTION SPECTRA OF NITROBENZENE IN VARIOUS SOLVENTS

Solvent	Absorption maximum mμ
Hexane	252
Water	267
69.6% H_2SO_4	276
98.4% H_2SO_4	288.5

carbon tetrachloride. From this the authors deduced that in more concentrated solutions nitromethane was present as a dimer, while in dilute solutions it is a monomer. Thus there is a state of equilibrium between the two forms:

$$2CH_3NO_2 \rightarrow (CH_3NO_2)_2 \quad (3)$$

Brand and his co-workers [17] carried out extensive studies on the absorption spectra of aromatic compounds in sulphuric acid solutions, i.e. in a strongly protonizing solvent. They found that under the influence of the sulphuric acid the maximum of the nitro group shifted. These shifts were most pronounced in the case of mononitro compounds, and the least in the case of trinitro compounds. They were smaller when sulphuric acid was used as a solvent, and larger when oleum was used. The absorption curves for 2,4-dinitrotoluene are shown in Fig.

42, and those for 2,4,6-trinitrotoluene in Fig. 43. The observation is in agreement with Hantzsch's old view (p. 218), that assumed nitrotoluene to possess a basic character, which appears when it is dissolved in sulphuric acid. Later studies have

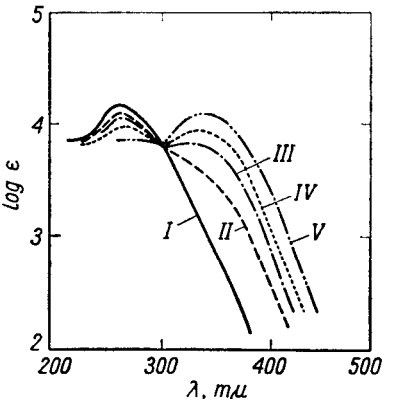


FIG. 42. Absorption spectra of 2.4-dinitrotoluene in sulphuric acid of various concentrations: I - 99.0, II - 102.74, III - 105.46, IV - 107.30, V - 114.5% H_2SO_4 (Brand [17]).

shown that as the number of the nitro groups increases, the basic properties weaken.

(On the addition of a proton to nitro compounds see also the chapter on the reactivity of aromatic nitro compounds, p. 218.)

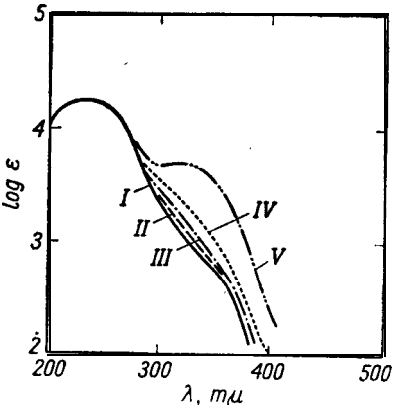


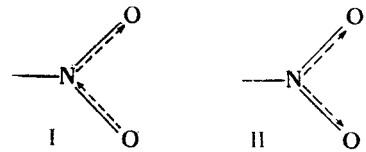
FIG. 43. Absorption spectra of 2,4,6-trinitrotoluene in sulphuric acid of various concentrations: I - 99.0, II - 102.1, III - 105.5, IV- 108.3, V- 114.5% H_2SO_4 (Brand [17]).

Mention should also be made of recent work of Tanaka [18], who has applied wave mechanics to calculate the σ– electron orbitals (two orbitals) and π– electron orbitals (one orbital with two electrons and two with one electron) of the nitro group. From these figures the author inferred that the absorption of the nitro

group near 280 mμ arises from the transition of free electrons surrounding oxygen atoms to the π orbital.

INFRA-RED ABSORPTION SPECTRA

In the infra-red region the nitro group produces two bands of high intensity: one near 6.4μ (1563 cm^{-1}), which characterizes asymmetric vibrations of the bonds of the nitro group (I), and another near 7.4μ (1351cm^{-1}), which characterizes symmetric vibrations of the bonds of the nitro group (II).



In addition to this, vibrations of the nitro group ranging from 4.0-4.17μ (2500-2398 cm^{-1}) exist (Kornblum, Ungnade and Smiley [19]), but they are of little significance for identification according to the authors.

On the basis of their investigations of nearly 35 nitro compounds, Kornblum, Ungnade and Smiley have distinguished the vibrations of primary, secondary and tertiary nitro groups in aliphatic nitro compounds (Table 23).

TABLE 23

Nitro compounds	Vibrations			
	asymmetric		symmetric	
	μ	cm^{-1}	μ	cm^{-1}
primary	6.45±0.01	1550±2	7.25±0.02	1379±3
secondary	6.45±0.01	1550±2	7.37	1357
tertiary	6.51±0.01	1536±2	7.41±0.02	1348±3

It can be seen from these data that the position of the nitro group band depends on whether the group is primary, secondary or tertiary.

The results of the above investigations are at the same time a summary of the earlier data obtained by several authors: Barnes et ***al. [20],*** Smith et *al.* ***[21],*** Haszeldine ***[22]*** and Brown [23].

Bellamy [24] gives the figures:

1565-1545 cm^{-1} and 1383-1360 cm^{-1}

for both primary and secondary nitroaliphatic compounds. In tertiary nitro compounds the frequencies are lower:

1545-1530 cm^{-1} and 1358-1342 cm^{-1}

Conjugation of the nitro group by attachment to an ethylenic double bond leads to a fall in both frequencies, according to Shechter and Shepherd [25] and Brown [23], to

1524-1515 cm^{-1} and 1353-1346 cm^{-1}

α– Halogen substitution has also a marked effect upon nitro group frequencies. According to Brown and Haszeldine the frequencies increase under tie influence of the α– chlorine atom.

They are: 1575±5 cm^{-1} and 1348±6 cm^{-1}, while under the influence of two α– chlorine atoms they are displaced:

1587±10 cm^{-1} and 1332±5 cm^{-1}

According to T. Urbanski [26] the bands of the nitro group in aliphatic nitro compounds under the influence of the hydrogen bond can be shifted to lower frequencies :

for asymmetric vibrations by	12-24 cm^{-1}
for symmetric vibrations by	30-42 cm^{-1}

Aromatic nitro compounds have been the subject of investigation by numerous authors: France1 [27], Lothrop et al. [28], Randle and Whiffen [29], and Brown [23].

Kross and Fassel [30], on the basis of investigation of over thirty aromatic compounds, gave the following vibration frequencies of the nitro group:

asymmetric: in non-polar solvents	1523±8 cm^{-1}
as solids	1525±10 cm^{-1}
symmetric: in non-polar solvents	1344±7 cm^{-1}
as solids	1339±7 cm^{-1}

These bands shift under the influence of several factors.

According to Brown [23], Kross and Fassel [30] and Conduit [7], the asymmetric frequence is considerably reduced from cu. 1534 cm^{-1} (e.g. to 1510 cm^{-1}) under the influence of a powerful electron-donor such as NH_2.

Conduit classified the asymmetric frequencies according to the number of nitro groups :

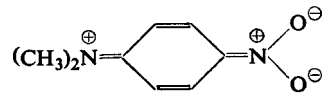
mononitro	1509-1540 cm^{-1}
dinitro	1539-1552 cm^{-1}
trinitro	1554-1567 cm^{-1}

The only discrepancy in the above correlation arises when a dinitro compound also contains strong electron-donor groups (e.g. NR_2.

Lippert [31] draws attention to the fact that the nitro group frequencies can be shifted under the influence of a solvent. They are decreased in polar solvents and their intensity increases. This effect is particularly strong when the nitro compounds contain strong electron-repelling groups. Thus *p*- nitrodimethylaniline gives bands in non-polar CCl_4 and strongly polar CCl_3CN as shown below:

	CCl_4	CCl_3CN
asymmetric vibrations	1506 cm^{-1}	1332 cm^{-1}
symmetric vibrations	1496 cm^{-1}	1320 cm^{-1}

Lippert [31] tried to explain this phenomenon by assuming that a polar solvent enhances the stability of the resonance structure of a solute

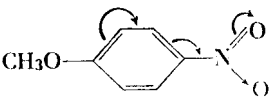


An increase in the number of molecules of this polar structure results in increasing the negative charge of the acceptor group, i.e. NO_2, hence in a decrease of frequency and a rise of intensity of absorption.

A number of authors have found that conjugation of double bonds lowers the frequency of NO_2 bands. Shechter and Shepherd [25], Fieser et al. [32], Eckstein, Kraczkiewicz, T. Urbanski and Wojnowska [33] have all reported that this occurs with nitro-olefins.

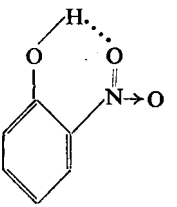
A similar phenomenon was noticed in the case of aromatic compounds. Thus, Bellamy [24] has pointed out that in polynitro compounds when one nitro group remains coplanar whilst another is twisted out of the plane of the ring under the influence of steric hindrance, the degree of aromatic conjugation is reduced and a new higher frequency band appears.

Frank, Hörman and Scheibe [34] also found that asymmetric NO_2 vibrations could be shifted towards lower frequencies under the influence of conjugation in aromatic compounds. They examined their substances in potassium bromide. A number of aromatic nitro compounds in dilute solutions were recently examined by T. Urbanski and Dabrowska [35]. They found that when a nitro group was placed in the *para* position with respect to another group, its symmetric stretching modes were of a lower frequency than in the *meta* position. This was most likely due to the strong conjugation of substituents with the ring:



The nitro group in the *ortho* position also gave a higher frequency. Thus for instance in the case of *o*-, *m*- and *p*- nitroanisoles the frequencies were 1352, 1347 and 1341 cm^{-1} respectively. In the case of *m*- and *p*- nitrophenol the frequencies were 1349 and 1339 cm^{-1} respectively.

The frequency of the nitro group in *o*- nitrophenol was markedly reduced, to 1320 cm^{-1}, as the result of hydrogen bonding between the nitro and phenolic group:



Bellamy [34] pointed out that in polyaromatic compounds multiple peaks can occur if hydrogen bonds are attached to the nitro group.

Steric effects of bulky substituents in the *ortho* position to the nitro group (such as I) can reduce the frequency of the *p*- nitro group vibrations, as shown by Perret and Holleck [36] (Table 24).

The authors explain that the strong steric effect on *o*- nitro groups produced by the halogens, particularly iodine, is superposed upon the induction effect of the *o*- nitro groups. Hence a reduction in the frequency of *p*- nitro group vibrations occurs. This is in agreement with an observation by Golder and Zhdanov [37] who

TABLE 24

Substances	Asymmetrical vibrations, cm^{-1}	Position of the nitro group
sym-Trinitrobenzene	1558	*o*- and *p*-
Picryl chloride	1550 1560	*p*- *o*-
Picryl iodide	1543 1558	*p*- *o*-

found that the C-N bond in the *para* position in picryl chloride is considerably shortened (1.38 Å), and thus approaches the value of a double bond. The *ortho*-situated C-N bonds are of a normal length (1.46 Å).

In the case of 2,4,6-trinitrobenzoic acid, the frequency of all the nitro groups remains unchanged (1553 cm^{-1}). However, the presence of nitro groups increases the C=O frequency of the carboxylic group to 1733 cm^{-1} (as against 1698 cm^{-1}

TABLE 25

SPECTRAL CHARACTERISTICS OF MONO-, DI- AND TRINITRO COMPOUNDS

Nitro compounds	Bands, cm^{-1}
o- Mononitro containing any one of the following groups *ortho* to the nitro: CH_3, C_2H_5, CHO, NH_2, COOH	787-781
p- Mononitro containing the same group as above *para* to the nitro	1111
m- Dinitro containing the following additional group: CH_3, C_2H_5, OH, $NH\text{-}NH_2$, COOH, CHO. OCH_3, CH_3NH, C_2H_5NH, NO_2 (trinitro) in sym-trinitro compounds	930-922† 939-909
m- Dinitro containing other additional groups *ortho* to the nitro	840-836
sym-Trinitro which have the additional groups: CH_3, C_2H_5, OH, OCH_3, OC_2H_5, COOH, NH	1081†

† **These bands are the most important for diagnostic purposes.**

in benzoic acid). According to Perret and Holleck [36], this is due to the out-of-plane deformation vibrations of the carboxylic group which occur under the influence of the nitro groups.

An extensive study of the infra-red absorption spectra of nitro compounds was reported recently by Pristera, Halik, Castelli and Fredericks [37a]. The following are bands which are valuable in the structural investigation of unknown nitro compounds and their mixtures (Table 25).

Recently a number of authors (Holder and Klein [38], Ogg Jr. and Ray [39] have examined certain nitro compounds, particularly in comparison with the nitrite ion (NO_2^-).

NUCLEAR MAGNETIC RESONANCE AND X-RAY EXAMINATION OF NITRO COMPOUNDS

The major application of nuclear magnetic resonance spectroscopy to organic chemistry involves the study of proton shifts (the "chemical shift" of proton),

The aromatic proton frequencies of substituted benzenes fall between 2.0 and 3.5 according to the number and nature of the substituents. Corio and Dailey [39a] have examined a number of monosubstituted benzenes.

The proton frequency of benzene was found to be 2.73.

In nitrobenzene the frequencies of the *meta* and *para* protons are lowered by the figures of the same order (-0.30 and -0.42 respectively), whereas the *ortho* protons are of much lower frequency (-0.97).

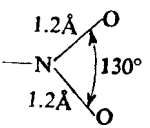
A similar phenomenon was found with COOH, COCl, $COOCH_3$ and CCl_3, whereas CN lowers the frequency by 0.30 equally in all three positions: *o-*, *m-* and *p-*.

Schmidt, Brown and D. Williams [40] examined the nuclear magnetic resonance of ^{14}N in three aromatic nitro compounds: nitrobenzene, nitrobenzoic acid, dinitrobenzoyl chloride.

In all three compounds the ^{14}N peak was observed. In each case the peak was not so wide as in NO_2^- ion and considerably wider than that in the NO_3^- ion. The broadness occurring with nitro groups (and even greater broadness in the NO_2^- ion) was indicative of large electric asymmetries at ^{14}N in these groups.

The shifts measured ranged from 165 milligauss in an ether solution of $(NO_2)_2C_6H_3COCl$ to 230 milligauss in $C_6H_5NO_2$, in a field of 10,700 gauss (NH_4^+ as a standard).

X-ray investigations indicate that the nitro group has a planar or near-planar structure, and that the atom distances and the bond angles for the nitro group of dinitrobenzene are:



The N-O angle for various compounds varies from 125° to 134°, and the distances between nitrogen and oxygen atoms from 1.17 to 1.30Å

The structural configuration of *p*- dinitrobenzene was the one most fully examined in investigations of the structures of aromatic compounds by X-rays. Among the first to carry out this research were Hertel [41], Bannerjee [42] and James, King

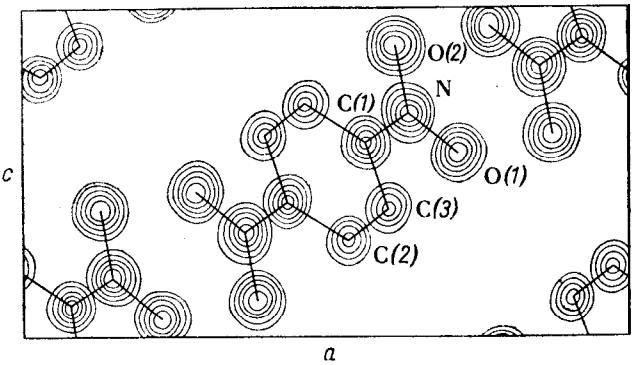


FIG. 44. Electrons density of *p*- dinitrobenzene(Llewellyn [44]).

and Herrocks [43]. The last group of investigators determined the structure by means of two-dimensional series and projections onto the principal planes. Because of limited accuracy attainable with the technique all that time the pattern obtained was not clear enough. The molecule was not planar, the benzene ring was distorted, and the N-O, bonds differed in length. It was only when Llewellyn's investigations [44] were published in 1947, in which a complete three-dimensional Fourier synthesis was applied, that a definite pattern was obtained as shown in

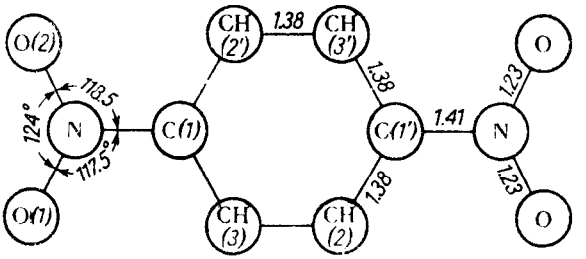


FIG. 45. Bond distances and angles of p-dinitrobenzene (Llewellyn [44]).

Fig. 44. The accuracy of determination of the bond length was ±0.02Å and that of the angles ±2°. The molecule proved to be exactly planar with the benzene ring undistorted, and the lengths of the N-O. bond equal.

The structure of m-dinitrobenzene has been established by X-ray analysis by Archer [45], utilizing Fourier analysis. The author proved the benzene ring to be a regular hexagon with sides of 1.41Å. The C-N bonds do not lie in the plane of the ring but make an angle of 15° with it. The C-N bond length is 1.54Å

and the N-O distance has been found to be 1.20 Å. The distance between the atoms of oxygen in the nitro group is 2.17 Å.

The structure of *m*- dinitrobenzene, as established by Archer [45], is shown diagrammatically in Fig. 46.

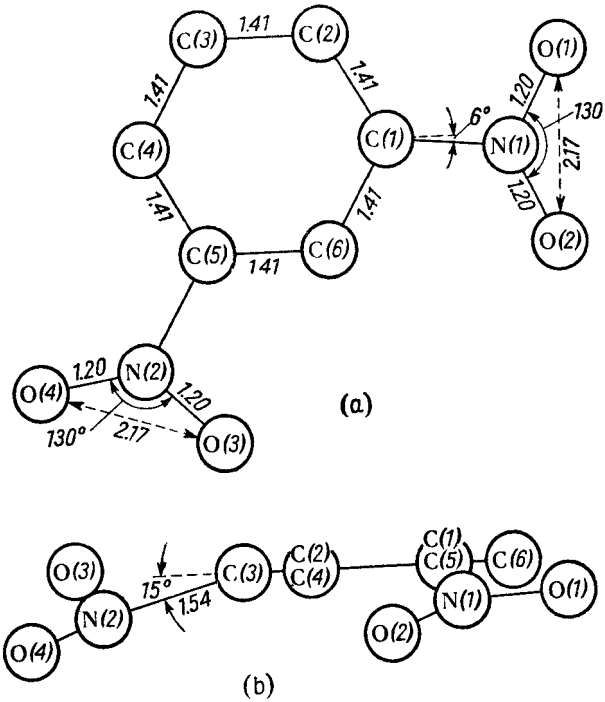


FIG. 46. Bond distances and angles of *m*- dinitrobenzene (Archer [45]).

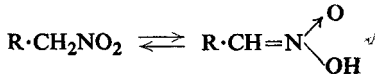
Structures of the simplest compounds containing the nitro group, such as for example, NO_2, N_2O_4, HNO_3 and NO_2^+, have already been discussed. The N-O distances for nitromethane are 1.21 Å and the bond angle 127° (Brockway, Beach and Pauling [46] and Rogowski [47]).

CHEMICAL PROPERTIES OF NITRO COMPOUNDS

PRIMARY, SECONDARY AND TERTIARY NITRO COMPOUNDS

The chemical properties of primary and secondary nitro compounds differ considerably from those of tertiary nitro compounds. This is due to the presence of active hydrogen atoms in the first two. The difference appears most clearly when nitro compounds are treated with alkalis. As long ago as 1872 Meyer [48,48a] observed that certain nitroparaffins were soluble in sodium hydroxide solutions. In 1888 Michael [49], and later Nef [50], suggested that the salt formed in the

process was one of the tautomeric forms assumed by the nitro compound, so-called aci- or iso-nitro form (Ia):

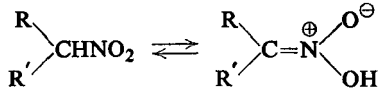


I Ia

Experimental evidence of the existence of aci-forms has soon been provided. In 1895 Holleman [51] found that *m*- nitrophenylnitromethane yielded a yellow salt, which under the influence of hydrochloric acid was converted initially into a yellow substance having a high electrical conductivity. After some time, the product changed into a colourless substance, showing no electrical conductivity. The aci-structure was assigned to the yellow substance, and that of a pseudoacid to the colourless one.

This observation was confirmed by Hantzsch and Schultze [52] in 1896 with phenylmtromethane. The aci-form of phenylnitromethane is a crystalline product. Its melting point is 84°C. It charges spontaneously into the normal, liquid form. Aci-forms differ from the normal ones in that they turn brown-red with ferric chloride.

Secondary nitroparaffins behave similarly :



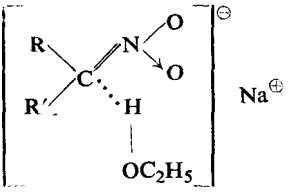
II Ha

Thus the anion of the aci-form of nitroparaffins can be written in two ways: IIIa and IIIb

IIIa IIIb

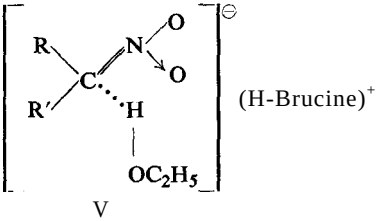
However, these structures were in doubt for a number of years. Strong evidence for criticizing them was given in 1927 by Kuhn and Albrecht [53]. They reported that optically active D- and L-2-nitrobutanes can be converted into their optically active sodium salts and then regenerated without complete racemization. This was confirmed by Shriner and Young [54] who found that 2-nitrooctane behaves similarly. Subsequently the structures Ia and IIa for the aci-forms and IIIa and IIIb for the aci-anion appeared to be excluded as they cannot correspond to dissymmetric configurations. If they were correct, the regenerated nitro compounds should be racemic.

Shriner and Young tried to explain this behaviour of nitroparaffins by postulating the “normal” structure of anion “stabilized” by combination with the solvent, e.g. ethanol, through a hydrogen bond (IV):



IV

This appeared to be supported by the findings of Ray and Palinchak [55] who resolved 9-nitro-2-benzoylfluorene with brucine. The brucine salt contained alcohol of crystallization and could probably be represented by the formula V:



V

The theory of "solvated asymmetric anion" therefore appeared to be admissible [56].

However, in 1947 Kornblum et al. [57] showed that the apparent incompleteness of racemization is due to incomplete neutralization and also to the presence of optically active impurities in the nitro compounds used. He found that the complete neutralization of the pure nitro compounds always leads to complete racemization. This was also confirmed by Theilacker and Wendtland [58]. The results of Komblum and the latter authors evidently supports the formulae Ia and IIa.

Generally speaking it is now admitted that primary and secondary nitroparaffins exist in normal and aci-forms and that there is an equilibrium between them.

The two forms may be distinguished from each other by the fact that aci-form absorbs bromine and gives characteristic colour reaction with ferric chloride. The equilibrium constant depends on the solvent used, and mainly on its basicity. Thus *p*- nitrophenylnitromethane contains 0.18% of aci-form in ethyl alcohol, 0.79% and 16% in aqueous methyl alcohol and pyridine respectively [59].

Tertiary nitro compounds, of course, do not undergo tautomeric transformation, and they might be expected to be resistant to alkalis. Nevertheless aromatic nitro compounds, and polynitro-ones in particular, are very sensitive to alkalis, and undergo transformation when treated with them. For example, sym-trinitrobenzene and also α– trinitrotoluene, when reacted with potassium hydroxide in methyl alcohol solution, form dark addition products (see also p. 202). Under certain conditions the nitro group can break off to form high molecular compounds.

Nitro derivatives of benzene, when boiled with sodium hydroxide in methyl alcohol solution are reduced to azoxy compounds (pp. 31, 237, 251). Nitro derivatives of toluene under these conditions are oxidized to nitro derivatives of stilbene (pp. 70, 283, 302).

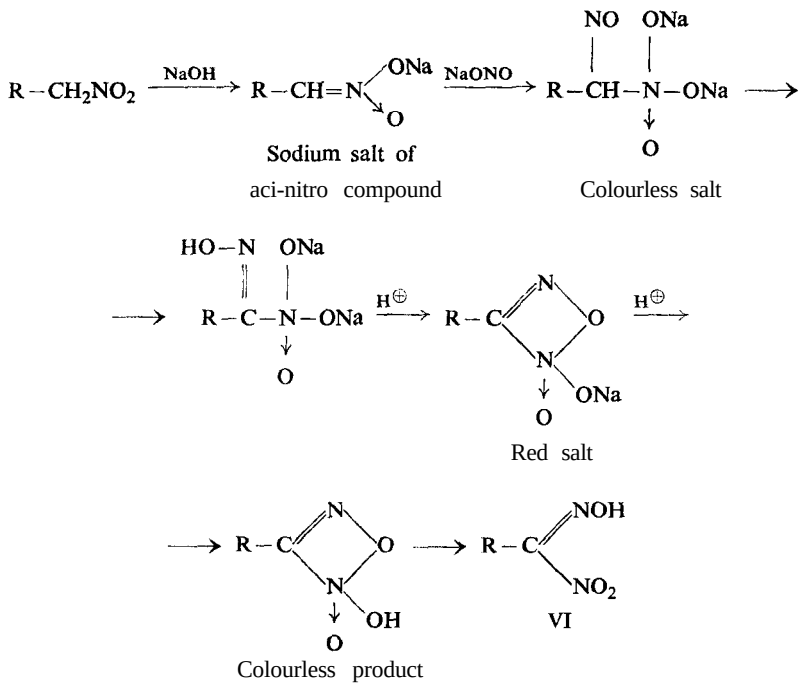
Both cryometric (Gillespie [60]) and spectrographic (Brand, Horning and Thornley [17]) investigations of nitro compounds indicate that in sulphuric acid solutions mononitro compounds behave like weak bases (p. 174). Thus it follows from cryometric measurements that nitromethane in 100% sulphuric acid solution is 20% ionized, and nitrobenzene 40%. Nitrobenzene is a stronger base than nitromethane.

The pale yellow colour of nitrobenzene or *p*- nitrotoluene turns more intense when the compound is dissolved in sulphuric acid, while solutions of nitromethane and other nitroparaffins are colourless. The yellow colour of the aromatic nitro compounds is due presumably to an ionic structure containing a quinonoid ring.

Primary and secondary nitro compounds also react with acids, while tertiary compounds show considerable resistance to them.

Primary nitro compounds, when treated with nitrous acid, give nitrolic acids (VI).

The reaction leading to the formation of nitrolic acids was described for the first time by V. Meyer [49]. The compounds are formed by treating aci-forms of primary paraffins with $NaNO_2$, followed by acidification of the whole mass. According to Veibel [61], the mechanism of the reaction may be presented by the following multistage scheme :

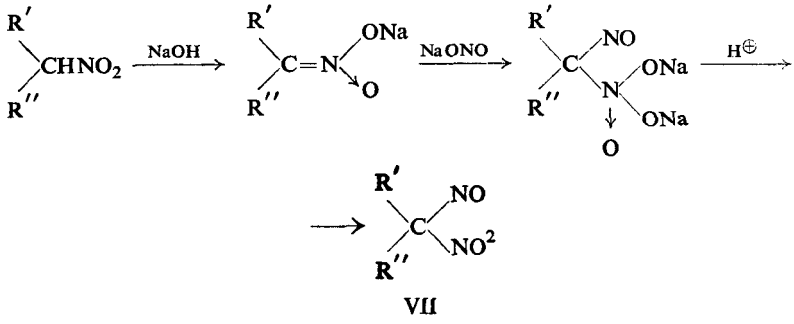


(4)

Nitrolic acids, when reacted with sodium or potassium hydroxide, produce a reddish-brown colour. The reaction is used for the detection of primary nitroparaffins. Secondary. nitroparaffins form pseudonitroles with nitric acid (VII)

Again V. Meyer was the first to describe the reaction. As in the formation of nitrolic acids, here also it is the aci-form of the secondary nitro compound that takes part in the reaction. It reacts with sodium nitrite to give a compound which. after acidification, forms pseudonitrole.

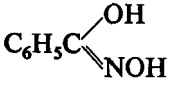
According to Veibel [61], the formation of pseudonitrole can be explained by the following reaction series :



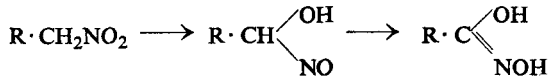
VII (5)

Pseudonitroles are crystalline, colourless products. They exist probably as dimers. But when molten or in solutions they turn blue, and are probably present as monomers. The reaction is utilized for the detection of secondary nitro compounds.

Heating the primary nitroparaffins with sulphuric acid of a concentration over 50% results in their isomerization to hydroxamic acids (IX).

From phenylnitromethane, Bamberger [62] obtained benzhydroxamic acid, 

and explained the mechanism of the isomerization reaction as:



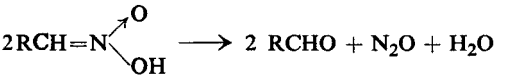
VIII IX (6)

A blue hydroxynitroso compound (VIII) is formed as an unstable Intermediate product.

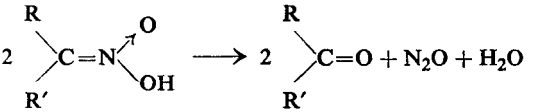
T. Urbanski [63] and T. Urbanski and Gurzydska [64] found that isomerization also occurs under the influence of acetic anhydride or ketene in the presence of a basic agent such as sodium acetate or pyridine.

In some cases hydroxamic acid hydrolyses to form hydroxylamine. The reaction has been utilized by Turski [65] for direct amination of aromatic hydrocarbons. Primary nitroparaffins were used in place of hydroxylamine, and sulphuric acid and a catalyst (e.g. V_2O_5) were present.

When a salt of the aci-form of a primary or secondary nitroparaffin is treated with an acid, it may decompose, evolving nitrous oxide and yielding an aldehyde or ketone:



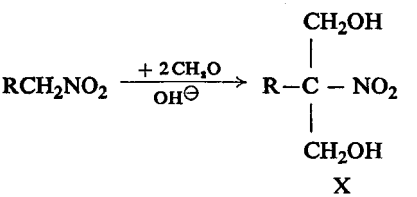
(7a)



(7b)

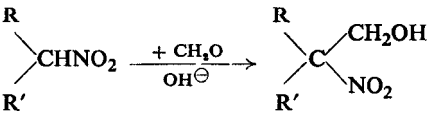
The reaction was discovered by Nef [50] and was investigated later by Nametkin [66], and by Johnson and Degering [671.

A very characteristic feature of primary and secondary nitro compounds is their ability to add on aldehydes in a weak basic medium to form nitroalcohols (X, XI). Formaldehyde is particularly readily added:



(8a)

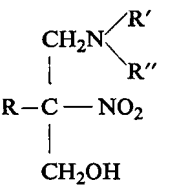
X



(8b)

XI

Nitroalcohols X and XI may be utilized as starting materials for the manufacture of nitric acid esters having explosive properties (see Vol. II). In the presence of primary or secondary amines or ammonia the reaction leads to formation of aminonitroalcohols (XII)



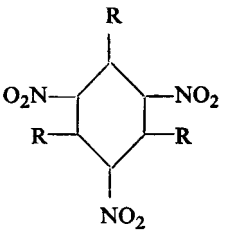
XII

When R' = H (i.e. in the case of primary amines), the product may react further with formaldehyde to form a tetrahydro-1,3-oxazine ring, or with an amine and formaldehyde to form a hexahydropyrimidine ring. When using ammonia, (R' = R" = H), the same rings may be formed (Hirst, J. K. N. Jones, T. Urbanski *et al.* [68]).

All nitro compounds, even the tertiary ones, which contain no "active hydrogen" atoms, react with the Grignard reagent (Oddo [84]). Thus, according to Gilman and Fothergill [69], nitrobenzene reacts in the Zerevitinov reaction as if it contained two active hydrogen atoms. Further studies of Gilman and Fothergill have proved

that the nitro group itself gives the Zerevitinov reaction, even when a compound does not contain hydrogen at all, as for example, tetranitromethane, pentabromonitrobenzene, etc.

According to several authors (e.g. Moureu [85], Bewad [86], Kharasch and Reinmuth [70]), the Grignard reagent may react with nitro groups reducing them to amino- or hydroxyamino groups (NHOH). However, this is not the only way the Grignard reagent reacts with aromatic nitro compounds. Thus Severin [71] has established that sym-trinitrobenzene reacts with magnesium alkyl bromide to form a yellowish precipitate of an addition product which, with aqueous acetic acid, gives colourless crystals of 1,3,5-tri-alkyl-2,4,6-trinitrocyclohexane



R = C_2H_5 (m. p. 276°C)

R = C_4H_9 (m. p. 258°C)

Polarographic reduction of nitro compounds is a subject matter of a recent monograph by Strading [87].

HETEROCYCLIC NITRO COMPOUNDS

Heterocyclic nitro compounds have no practical importance in the technology of explosives, either because the raw materials are too expensive, or because it is difficult to introduce the nitro group into them. For example, pyridine and its homologues, the most easily obtainable heterocyclic compound, are nitrated only with the greatest difficulty, and the most powerful nitrating agents give 3-nitropyridine only in low yield (e.g. 6%) [89].

When nitrated in the gaseous phase with nitrogen dioxide at temperatures of 115-120°C, pyridine gives also 3-nitropyridine (Shorygin and Topchiyev [74]) in the same yield. See also Schofield [90].

Alkylpyridines (picolines, and especially lutidines) can be nitrated much more readily, as Plazek [75] has shown. Introduction of the nitro group is greatly facilitated by the presence of the hydroxyl group in the pyridine ring. For example, 3-hydroxypyridine can be nitrated to 2-nitro-3-hydroxypyridine in good yield (Plazek and Rodewald [76]). It may be further nitrated to the dinitro derivative. From this, 3,5-dinitropyridine can be obtained (Plazek [77]).

It has been shown recently by den Hertog and Overhoff [78] that N-pyridine oxide can readily be nitrated with a nitric and sulphuric acid mixture. 4-Nitropyridine is formed in good yield-about 81%.

Another heterocyclic compound obtainable in considerable quantities-quinoline-nitrates in the isocyclic ring. Indole and carbazole behave in a similar way. Nitro derivatives of these compounds have not yet found practical application.

Dinitro derivatives of thiophene described by Steinkopf have recently been obtained in a pure form by Blatt and co-workers [80] by nitrating 2- and 3-nitrothiophenes in nitric acid-acetic anhydride mixture, according to Steinkopf. A good yield of 2,4-dinitrothiophene (m.p. 49-50°C) was obtained. In the case of nitrating 3-nitrothiophene a smaller proportion of 2,5-dinitrothiophene (m.p. 78-82°C) was also formed.

The ability of the substances of being nitrated depends on many factors which exercise their influence upon the activity of the compounds. For example cyclopentadiene, C_5H_6 can readily be nitrated with ethyl nitrate (Thiele [72]). Titov [73] explained this fact by suggesting that the hydrocarbon forms readily the anion $C_5H_5^-$ which possesses a high potential π.

On the contrary, ferrocene, $(C_5H_5)_2Fe$, can be nitrated with difficulty. This is explained by formation of cation $(C_5H_5)_2Fe^+$ with reduced activity towards electrophilic agents.

NITRO COMPOUNDS AS EXPLOSIVES

Among aliphatic nitro compounds nitromethane was only recently recognized as an explosive. Tetranitromethane is not explosive but can form an explosive when mixed with combustible substances. Tetranitromethane possesses here a character of an oxygen carrier.

Nitro derivatives of aromatic compounds as explosives are of greatest practical importance.

It is usually considered that only those nitro compounds possess explosive properties which contain at least two nitro groups attached to one benzene ring. However, Berthclot [81] noticed as long ago as 1887 that the presence of even one nitro group is sufficient to increase the ease of thermal decomposition of the aromatic compound. This was later confirmed by Datta and Chatterjee [82], and Condit and Haynor [83] when studying the temperatures of thermal decomposition of nitro compounds. Nevertheless, among aromatic nitro compounds only those which have three or more nitro groups for one benzene ring (and some of those which have two) exhibit distinctly marked explosive properties. Among the compounds with two nitro groups, only dinitrobenzenes and dinitrotoluenes are recognized as explosives while dinitronaphthalenes are on the borderline between explosive and non-explosive substances. Trinitronaphthalene has explosive properties similar to those of dinitrobenzene, since the ratio between the number of nitro groups and carbon atoms is approximately the same for both compounds.

For this reason, mononitro compounds will be described only from the viewpoint of their utilization as intermediates for the preparation of higher nitrated products.

Explosive nitro compounds exhibit a high degree of chemical stability and undergo no changes during storage. They differ from other explosives by possessing a low sensitivity to impact and friction.

Aromatic nitro compounds are obtained from the corresponding aromatic compounds by classic nitration methods using mixtures of nitric and sulphuric acids. The methods will be discussed in further chapters.

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CHAPTER VI

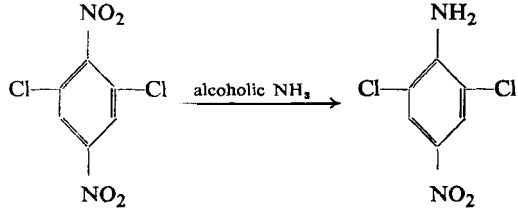
AROMATIC NITRO COMPOUNDS

REACTIVITY OF THE NITRO GROUP

Aromatic nitro compounds which are of course tertiary, form a separate group of compounds, differing from the aliphatic nitro derivatives in many respects. For this reason they deserve special attention.

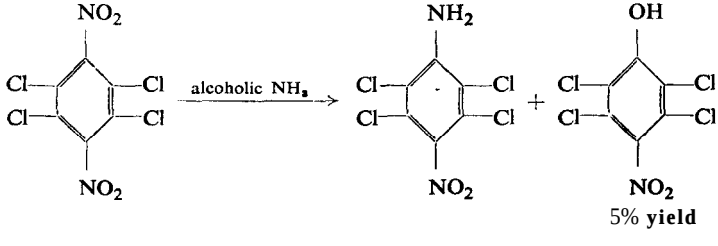
The attachment of nitro groups to the aromatic ring affects their reactivity. For example, nitro groups in *ortho* or *para* position in relation to each other are rather reactive, and one of them can be substituted relatively easily. Only the nitro groups in the *meta* position to each other are stable. Thus, one of the nitro groups in the unsymmetrical trinitrotoluenes (isomers of TNT) can readily be substituted. This is a consequence of the substitution rule, that the nitro group directs a new entrant group towards *meta* position. If in an aromatic compound two nitro groups, i.e. meta-orienting groups, are in a different - *ortho* or *para* position in relation to each other, the system must be unstable.

A nitro group may also become mobile under the influence of a large number of substituents in the same ring. The following reaction was observed by Körner and Contardi [l] as early as 1914:

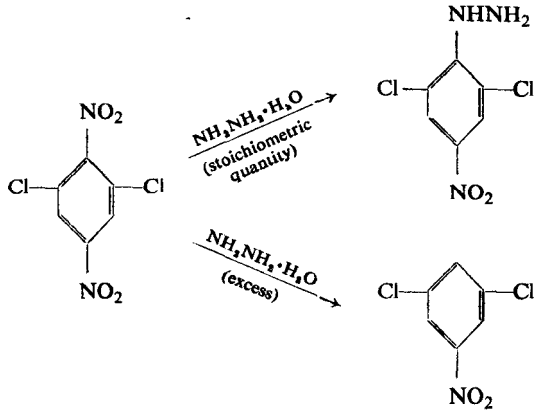


(1)

Peters, Rowe and Stead [2] observed a similar reaction, accompanied by hydrolysis as a side-reaction:

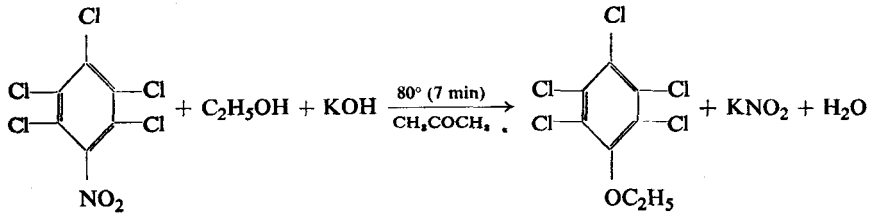


A number of reactions on the mobility of the NO_2 group have been carried out by Qvist and his co-workers [3,4,5]:



(3)

In presence of an excess of hydrazine, denitration occurs, probably because of the reducing action of this reagent. Pentachloronitrobenzene (a well known fungicide "Terraclor") hydrolyses to form pentachlorophenol or its ethers:



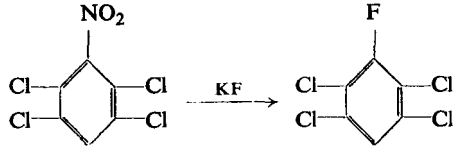
"Terraclor" Pentachlorophenetole

The yield of the reaction amounts to 50% and it can be utilized for quantitative analysis of pentachloronitrobenzene by determining the quantity of KNO_2 split off (Ackermann ***et al.*** [6]).

On mobility of nitro groups, see also Loudon and Robson [158].

Nitro groups can be replaced by chlorine and bromine on drastic action of phosphorous pentachloride (Ganguly [6a]) or chlorine [151] and bromine [152] respectively.

A nitro group adjacent to chlorine atoms in the *ortho* and *meta* position can be replaced by fluorine on heating with potassium fluoride at 147°C:



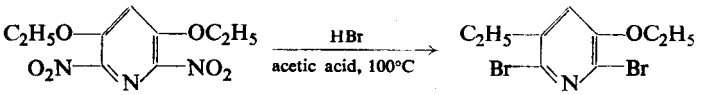
(5)

The reaction yield is 10%. It may be increased up to 37% by heating in dimethylformamide solution (Finger and Kruze [7].)

On vigorous reaction with basic reagents (sodium hydroxide or sodium alcoholate), a nitro group located symmetrically, in the *meta* position to other nitro groups

and, hence of relatively low reactivity, may also be substituted. Thus, for example, from sym-trinitrobenzene, 3,5-dinitrophenol or its ethers may be obtained (p. 251).

An interesting example of the replacement of a nitro group in the *meta* position by a bromine atom can be observed in the case of the pyridine derivatives (Koenigs, Gerdes and Sirot [8]):



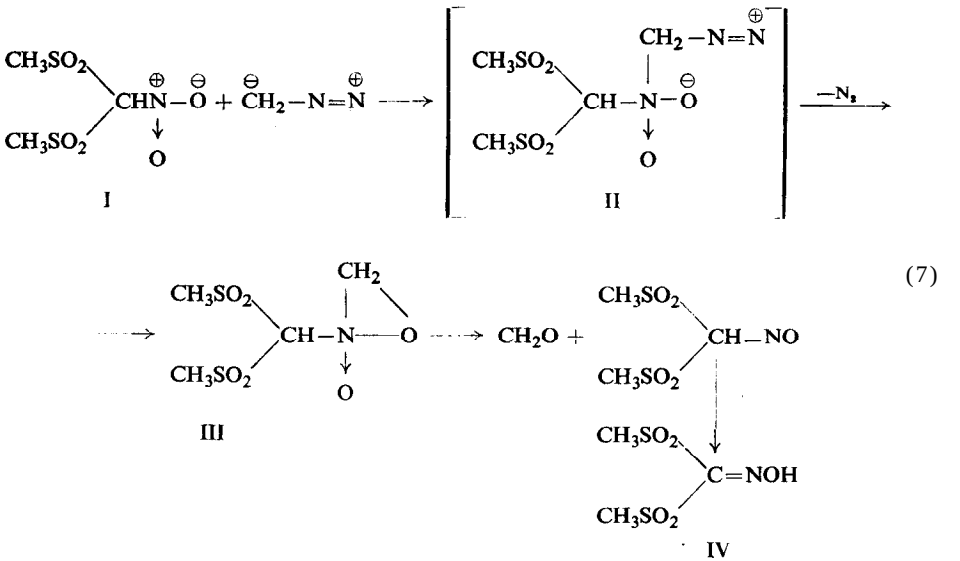
(6)

Also the nitro group in 4-nitropyridine-N-oxide is very mobile (den Hertog and Combé [8a]).

The nitro group itself exhibits a certain reactivity which is not confined to the liability to reduction or to the formation of addition products.

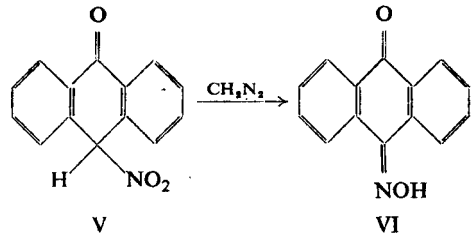
Thus, Backer [9] explained that in certain cases an aliphatic nitro group could react with such a typical methylating agent as diazomethane. For example, bis-(methylsulphonyl)nitromethane (I), when reacted with diazomethane, formed a crystalline product which was found to be an oxime (IV). Simultaneously formaldehyde was formed, doubtless from the methylene group of diazomethane.

Backer explained the reaction assuming the following mechanism:



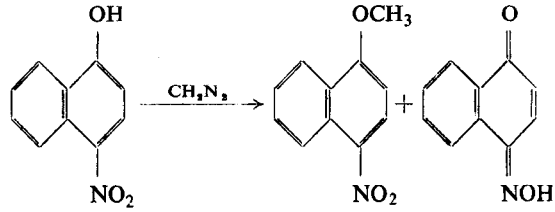
(7)

The observation that a nitro group of an aliphatic character in an aromatic molecule could react with diazomethane was confirmed by Edwards [10] for nitroanthrone, which reacted with diazomethane to form anthraquinone oxime (VI):



V VI (8)

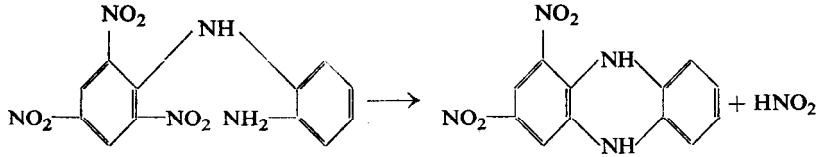
According to that author, such a typical aromatic nitro compound as 4-nitro-l-naphthol (VII) when reacted with diazomethane, formed not only methyl ether (VIII) but also quinone oxime (IX) in lower yield (16%):



VII VIII IX (9)

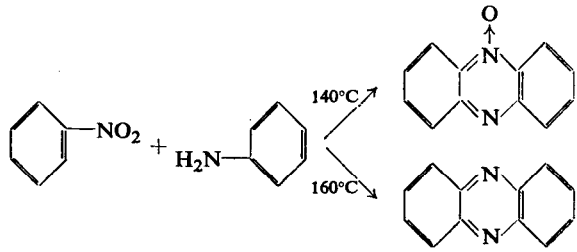
From these examples one could infer that diazomethane would react with those nitro compounds which contain a reactive hydrogen atom. With that respect particularly important is recent work of de Boer [160].

The nitro group can take part in the formation of heterocyclic nitrogen-containing rings. For example, one of the well known methods for the preparation of phenazine derivatives consists in heating derivatives of 2-nitro-2'-aminodiphenylamine at high temperature (Kehrmann et al. [11]) :



(10)

The synthesis of phenazine derivatives and phenazine oxide based on the condensation of aromatic nitro compounds with aromatic amines in an alkaline medium (sodium hydroxide), reported for the first time by Wohl [12] in 1901, was of similar character :

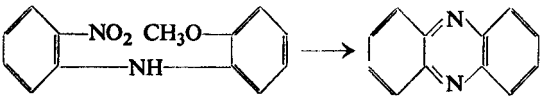


(11)

at 140°C phenazine and its oxide were formed, while at 160°C phenazine only was obtained. The yield of the reaction was insignificant.

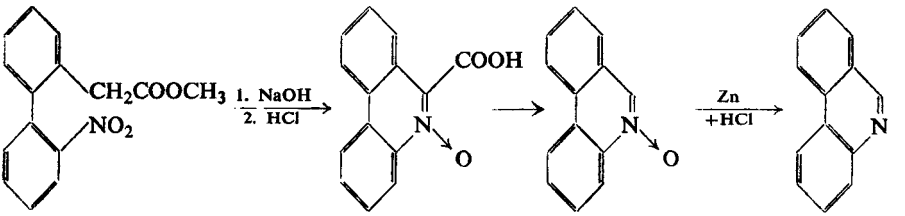
The reaction was improved and its mechanism partly elucidated by several Russian investigators (Pushkareva and Agibalova [13], Chernetskii, Kipryanov, Serebrianyi and others [14-17] and Abramova and Postovskii [18]).

It is interesting to note an example of cyclization by the elimination of a methoxy group by means of a nitro group (Slack and Slack [19]) :



(12)

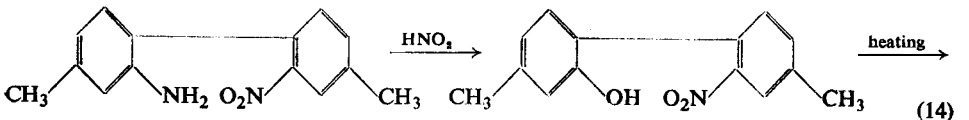
Among more recent examples of cyclization through a nitro group the reaction of preparation of phenanthridine might be referred to (Muth, Ellers and Folmer [20]) :



(13)

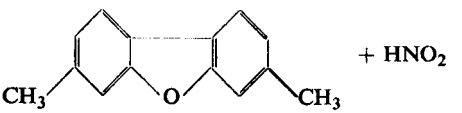
The known reduction of two nitro groups to an azoxy group by acting with strong alkali on nitro compounds (p. 183) can yield cyclic azoxy compounds, according to Knueppel [153].

A rather unusual example of cyclization by means of a nitro group can also be referred to in which the nitro group is separated as a molecule of nitrous acid (Turpin [20a], Angeletti and Brambilla [21]), e.g.:



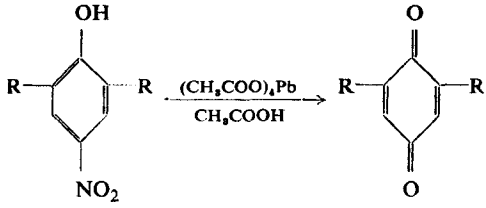
(14)

2-Amine-2'-nitro-4,4'-dimethyldiphenyl



3,7-Dimethyldiphenylene oxide

An interesting instance of elimination of a nitro group was given by Kenner and co-workers [21a,21b]. It consists in oxidation of 2,6-disubstituted derivatives of *p*- nitrophenol by lead tetraacetate at room temperature to form derivatives of *p*- benzoquinone in excellent yields:



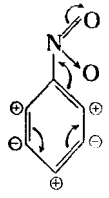
(15)

(R are alkyls)

The reactivity of the nitro group is also manifested by the ease of its reduction. Thanks to this, aromatic compounds (e.g. nitrobenzene) can be used as oxidizing agents in the well known Skraup reaction.

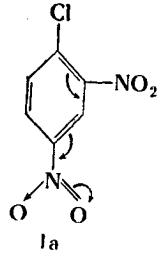
INFLUENCE OF NITRO GROUPS ON REACTIVITY OF HYDROGEN ATOMS AND SUBSTITUENTS. NUCLEOPHILIC REACTIONS

The fact that the nitro group is a meta-orienting one can be explained by the induction effect, caused by its electron attracting properties (I):



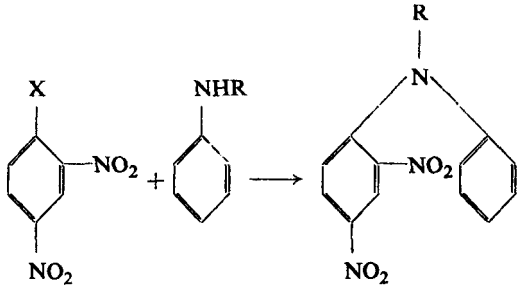
In practice, *ortho* and *para* substitutions also occur to a lesser extent along with the ***meta*** substitution in relation to the nitro group. Some deviations from the rule of substitution in the *meta* position are also encountered.

The nitro group has a considerable influence on the properties of the whole molecule of an aromatic compound. For example, owing to the presence of the nitro group, nitrobenzene does not take part in the Friedel-Crafts reaction. The reactivity of a chlorine atom, brought about by the presence of a nitro group in the *ortho* or *para* position, may be represented by a diagram based on the induction effect (Ia).



Ia

A halogen atom in the *ortho* or *para* position to the nitro group can readily undergo nucleophilic displacement. The higher the polarization ability of a halogen, the more readily it enters into substitution reactions. Therefore the common rule that the atoms of the lighter halogens are more reactive is not followed here. For example, the reaction of halogeno-2,4-dinitrobenzene with N-alkylaniline in nitrobenzene solution runs with the greatest rapidity in the case of bromine, and with the lowest in the case of fluorine, i.e. the reactivity varies according to the order: Br>Cl>F:



(16)

This was formerly considered to be one of the most typical examples of nucleophilic displacement.

However, several exceptions to this rule have recently been observed.

According to Beckwith, Miller and Leahy [22], the rates of the nucleophilic displacement of halogeno-2-dinitrobenzenes with sodium methoxide or sodium *p*- nitrophenate for the F, Cl, Br and I derivatives can be expressed by the figures 2880, 1, 0.690, 0.154 respectively.

However, this sequence may be altered as a result of changes in the nucleophilic agent and the solvent. Thus Hammond and Parks [23] noticed the rate of reaction of halogeno-2,4-dinitrobenzenes with aniline in ethanol to be the highest with fluorine and the lowest with chlorine : F> Br> Cl. When N-methylaniline in nitrobenzene solution was used the sequence was Br>Cl>F - as mentioned above (Fierens and Halleux [24]).

Temperature can also influence the rate of this nucleophilic displacement and alter the rate of reaction of different halogens. Brieux and Deulofeu [25] made the important observation that the temperature change may. affect the rate of reaction of various halogens differently. Thus the halogeno-2,4-dinitrobenzenes react with piperidine at the rates which can be arranged:

as Br>Cl>I at 75°C

and

as Br>I>Cl at 100°C

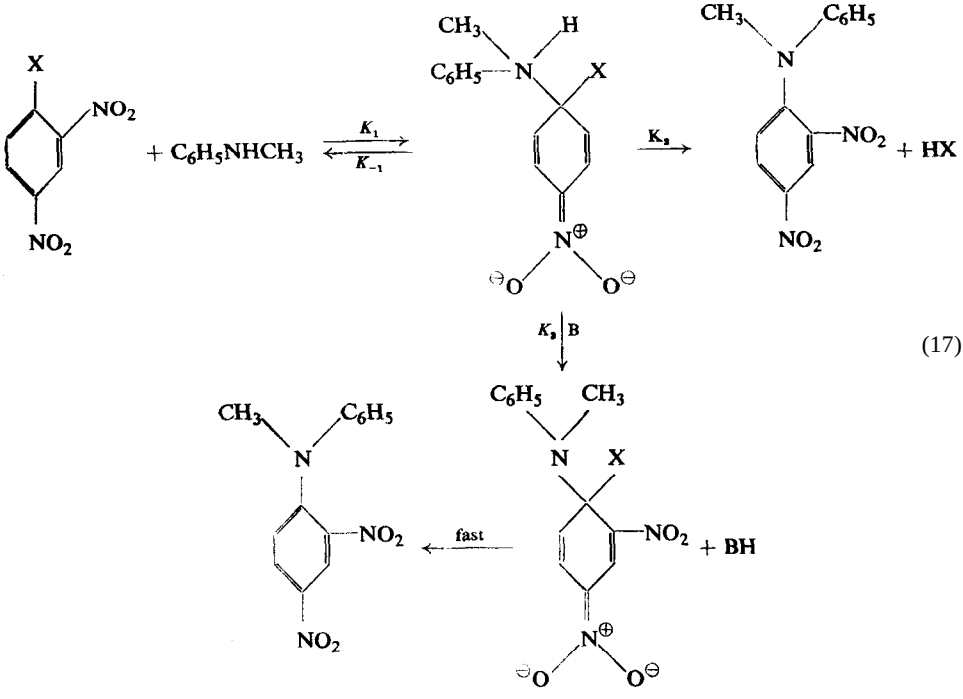
This would explain the discrepancy between the data of different authors. (Brewin and Turner [26] and Sandin and Liskear [27] examined the rate of reaction with piperidine in benzene. The temperature of a boiling solution in benzene is in the region where a change in the order of reactivities may take place.)

Plazek [28,28b] and Plazek and Talik [28a] stated recently that the reactivity of halogens in nitro derivatives of pyridine is much higher than in the similar benzene derivatives. Thus, at 20°C where only 0.5% of chloro-2,4-dinitrobenzene was subjected to nucleophilic displacement of chlorine by the amino group, the figure was 98.3% for 2-chloro-3,5-dinitropyridine.

In water, after 5 hr of boiling, the following figures for percentage reacted were recorded :

ca. 1.0%, of chloro-2,4-dinitrobenzene
26.2% of chloro-2,4,6-trinitrobenzene
98.4% of 2-chloro-3,5-dinitropyridine
99.7% of 2-bromo-3,5-dinitropyridine

Bunnet and Randall [29] suggest a two-stage mechanism involving a nucleophitic reaction of the formation of a metastable intermediate complex according to the diagrammatic presentation:



(17)

Bases (e.g. alcoholic potassium acetate) were found to catalyse the reaction when X= F, but they do not catalyse it when X= Cl.

Bunnet and Randall suggest the following equation for the rate of reaction K:

$$K = \frac{K_1K_2 + K_1K_3(B)}{K_{-1} + K_2 + K_3(B)}$$

(See also Knowles, Norman and Prosser [159]).

S. D. Ross [30] studied the nucleophilic displacement reaction in aromatic systems by examining the rate of reaction of chloro-2,4-dinitrobenzene with n-butyl-

amine and with OH^- in dioxane-water (50/50). The results suggest that the reaction with the amine is catalysed by both n-butylamine and OH^- ions.

Plazek and L. Kuczyriski [31] investigated the reactivity towards ammonia of bromine atoms in *o-*, *m-* and *p-* bromonitrobenzene. The bromine atom in a position *ortho* to the nitro group is the most reactive, while the bromine atom in the *meta* position is the least so. However, in the presence of copper catalyst ($CuSO_4.5H_2O$) there is not much difference between the reactivity of *meta-* and *para-* bromine atoms. The bromine atom in the *ortho* position remains the most reactive in the presence of a catalyst.

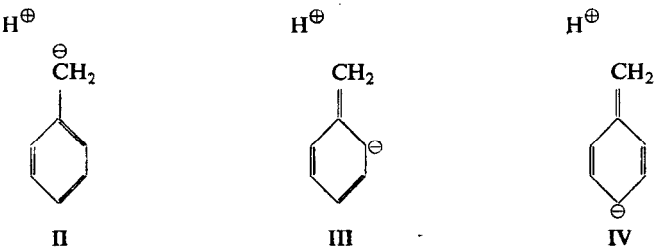
Hawthorne [31a] arrived at a similar conclusion when investigating the rate of reaction of *o-* and *p-* chloronitrobenzene with piperidine. The displacement of the chlorine atom from the *ortho* compound by piperidine at 116°C proceeds 80 times more rapidly than the similar reaction of the *para* compound. He also observed that substitution of D for H in the amino group in the nucleophile (piperidine) did not alter these rates of reaction.

Recently Reinheimer and his co-workers [31b] found that a number of salts have a marked effect on the rate of reaction of chloro-2,4-dinitrobenzene with sodium methoxide to yield 2,4-dinitroanisole. Thus, lithium salts slowed the reaction, sodium salts did not change the rate of reaction while potassium salts increased the reaction rate. These results were interpreted on the basis of the ion pairing of Na^+ and OCH_3^- ions in solution. Addition of another M^+ from added salt would affect the equilibrium

$$M^+ + OCH_3^- \leftrightarrow M\text{-}OCH_3$$

The carboxyl group of trinitrobenzoic acid is also mobile and can readily be liberated as CO_2 simply by heating.

The fact that nitro groups attached to an aromatic ring increase the reactivity of the hydrogen atoms of a methyl group, can also be explained by the induction effect strengthening the effect of hyperconjugation of the molecule of toluene. According to the concept of hyperconjugation, the ionized states of toluene can be written as II, III and IV:



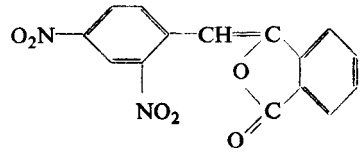
II III IV

(see for instance Waters [32], E. Müller [33]).

This would explain a number of reactions of the methyl group in nitro derivatives of toluene, particularly in trinitrotoluene. For example, formaldehyde can

be added relatively easily to the methyl group of trinitrotoluene, resulting in the formation of the trinitro derivative of phenylethyl alcohol (Vol. II).

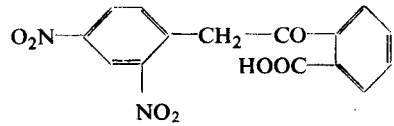
The methyl group in nitrotoluenes reacts with benzaldehyde much more readily than that of toluene itself, giving the corresponding derivatives of stilbene. Mono-, di- and tri-nitrotoluenes also react with *p*- nitrosodimethylaniline to form the corresponding anils. Such a product is not obtained in the case of toluene (Sachs and Kempf [34]). The methyl group of 2,4-dinitrotoluene also reacts with pyridine N-oxide in the presence of iodine to yield 2,4-dinitrobenzaldehyde [155]. Poray-Koshits and Chizhevskaya [35] found that di- and trinitrotoluenes react with phthalic anhydride to form nitro derivatives of benzylidenephthalide:



Mononitrotoluene is not subject to this reaction.

The compounds obtained are crystalline products and may be utilized for the identification of di- and tri-nitro compounds containing a methyl group.

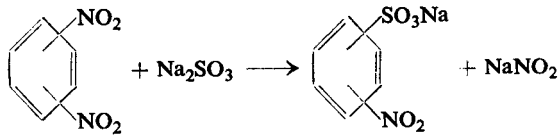
On heating with an aqueous solution of NaOH the benzylidenephthalide derivatives hydrolyse to form ketoacids:



2,4-Dinitrotoluene also reacts with pyridine and iodine to yield 2,4-dinitrobenzylpyridinium iodide [156].

On boiling nitro derivatives of toluene with sodium hydroxide, their methyl group is readily oxidized, forming a methine group and nitro derivatives of stilbene.

One of the typical reactions of aromatic nitro compounds with two or more nitro groups is that with sodium sulphite. Here one of the nitro groups is replaced by a sulphonic group (as its sodium salt) and sodium nitrate is formed:



(18)

The reaction occurs particularly readily with nitro groups that are in the o- and *p*- position to each other, i.e. with "mobile nitro groups". As to *meta*- nitro groups they react less readily and require a higher temperature. Nitro derivatives of higher homologues of benzene with two or three nitro groups (such as di- and tri-nitro derivatives of *m*- xylene also react less readily, and trinitromesitylene does not react with sodium sulphite [35a].

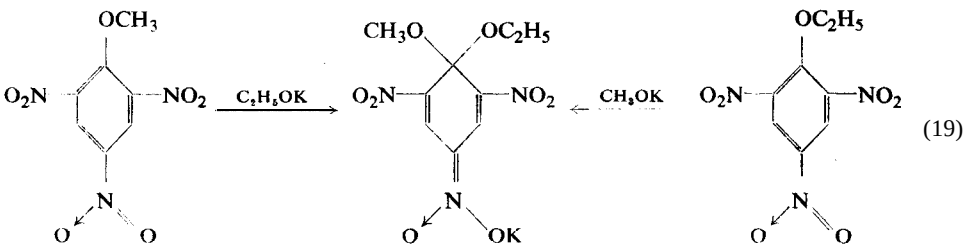
The reaction is of great practical importance and is described in detail in the appropriate places (pp. 231, 308, 332 and 379).

It is well known that the presence of nitro groups in aromatic amines makes diazotization of the amino group more difficult.

The presence of nitro groups in diazonium compounds considerably facilitates coupling to yield azo-compounds. For example the diazonium salt of picramide couples readily with mesitylene [157].

A nitro group attached to an aromatic ring may activate the ring. Owing to this the nitro-substituted aromatic ring can take part in reactions in which it usually remains more or less inactive. Nucleophilic reactions of nitro compounds should be mentioned here first.

Nitro compounds, particularly the higher nitrated derivatives, readily enter into nucleophilic reactions. The reactions of aromatic halogenonitro compounds with bases (p. 453), as well as the addition of potassium methoxylate on to sym-trinitrobenzene resulting in the formation of an anisole derivative will be discussed below. Similar addition reactions of potassium methoxylate to trinitrotoluene (p. 301) and trinitroanisole (p. 546) are also known. These reactions were described in detail by Meisenheimer [36-38]. Confirmation of such an interpretation of the reaction is provided by the fact that in the reaction of potassium ethoxylate with trinitroanisole the same dark coloured product (I) is obtained, as when potassium methoxylate is reacted with trinitrophenetole:



(19)

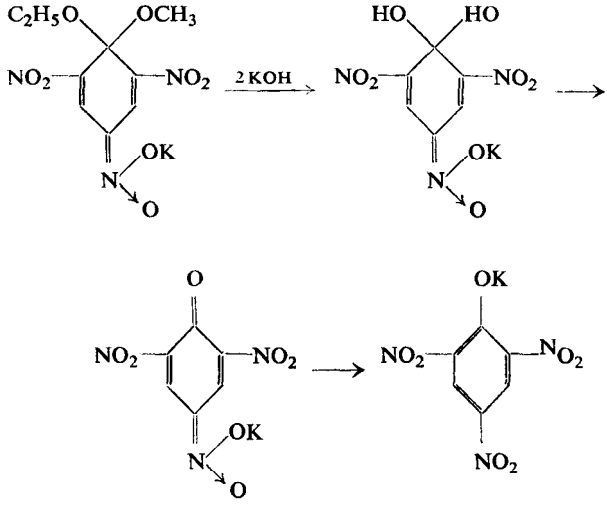
When treating the addition product (I) with dilute sulphuric acid, Meisenheimer obtained a mixture containing trinitrophenetole. Jackson and Earle [39] confirmed Meisenheimer's results as regards the preparation of the product.

Hammick and Foster [40] investigated the infra-red absorption spectra of the products obtained by both routes. The visible spectra were examined by Foster [41]. Both spectra were found to be identical in each case.

Gitis and Glaz [42] also confirmed Meisenheimer's view. They found that the ultra-violet spectrum of the addition product resulting from the reaction of potassium ethoxylate with trinitroanisole was identical with that of the addition product of potassium methoxylate and trinitrophenetole. Both products showed an absorption maximum at 485 mμ.

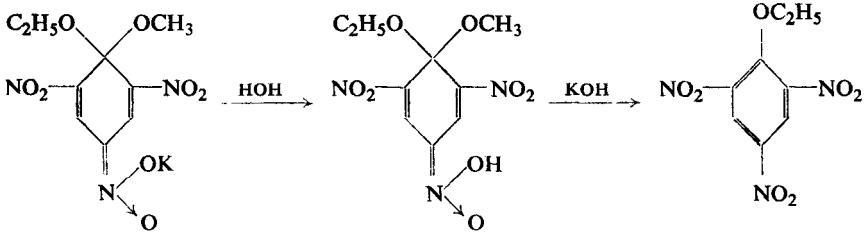
Moreover, the same authors found that heating the product with potassium

hydroxide resulted in the formation of potassium picrate, presumably according to the scheme:



(20a)

At a low temperature the reaction occurred without complete hydrolysis of the ether group, and the ethyl ether of picric acid was formed:



(20b)

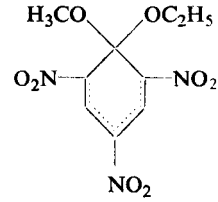
When products of the reaction of higher alcoholates with trinitroanisole were hydrolysed, ethers of higher alcohols were formed. According to the authors, this could be a convenient method of preparing higher ethers of picric acid.

The kinetics and mechanism of Meisenheimer's reaction has been studied by Caldin and Ainscough [43] who utilized the reactions of addition of sodium ethoxylate to trinitroanisole, trinitrobenzene and trinitrotoluene. By using temperatures in the range from -70°C to -100°C they were able to reduce the reaction rate to a measurable value. On treating the addition product with acetic acid at temperatures ranging from -50°C to -80°C they obtained the starting product. Thus, the reaction was proved to be reversible, as for example in the case of trinitroanisole (TNA) :

$$TNA + OC_2H_5^- \leftrightarrow [TNA, OC_2H_5^-] \leftrightarrow [TNA^-.OC_2H_5] \quad (21)$$

Addition product (II)

The authors consider that the addition product may exist as a complex, in which a transfer of charge has taken place, while the structure of the true addition product is III.



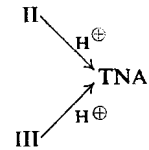
III

The reaction of the formation of product II is fast. while that of product III is slow:

$$TNA + OC_2H_5^- \leftrightarrow II$$

$$II \xrightarrow{slow} III$$

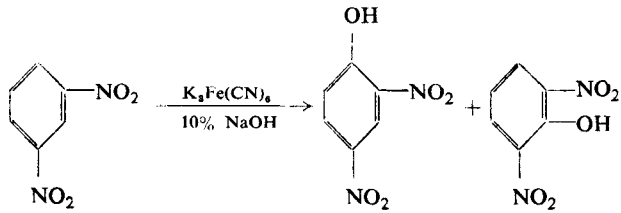
On treating both products, (II) and (III), with acetic acid the authors were able to regenerate the original nitro compound:



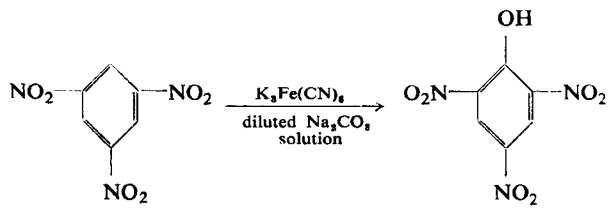
(22)

The products of type III obtained from various other nitro compounds, are discussed further under the heading of the individual nitro compounds (see also Farmer [44]).

Oxidation of nitro compounds to nitrophenols is another example of a nucleophilic reaction. Thus, *m*- dinitrobenzene and *sym*- trinitrobenzene were oxidized in an alkaline medium when boiled with potassium ferricyanide solution (Hepp[45]) :



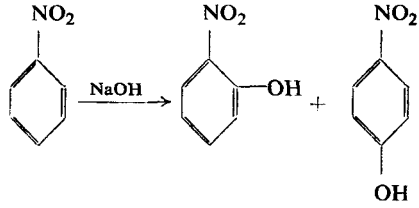
(23)



(24)

This reaction does not occur with nitrobenzene.

The oxidation of nitrobenzene to *o*- nitrophenol (with traces of the *p*- isomer) when mixed with dry sodium hydroxide, and slightly heated, may be another example of the oxidation of nitro compounds by nucleophilic substitution (Wohl [46]):

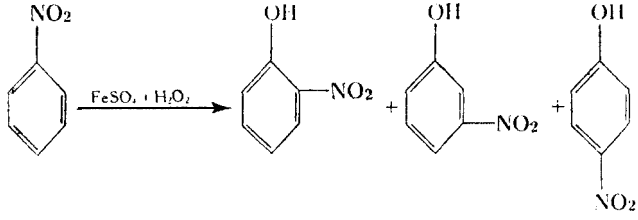


(25)

The yield of *o*- nitrophenol in this reactions amounts up to 50% of the theoretical value.

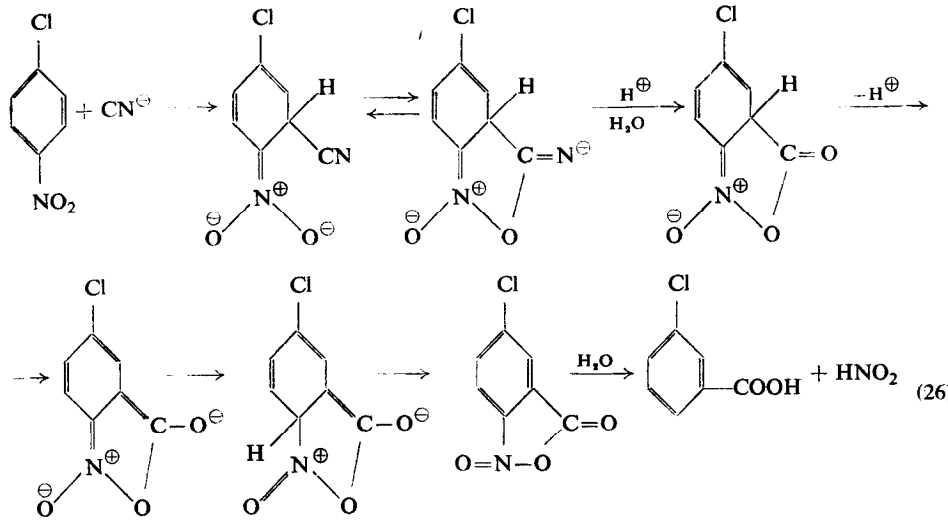
A specific feature of these reactions is that the substitution occurs in the ortho and *para* positions. This is typical of nucleophilic reactions whereas the *meta*-orienting influence of the nitro group (i.e. the conventional substitution rule) can be observed when electrophilic substitution occurs.

Another example of nucleophilic hydroxylation of nitro compounds is the formation of nitrophenols by the action on nitrobenzene with aqueous ferrous sulphate in the presence of hydrogen peroxide in a yield of *ca.* 3% [46a] (Fenton's reagent) [46b] ; Weiss *et al.* [46]) and by the action of ionizing radiations on aqueous solution (Weiss and Stein [46c]) *:*



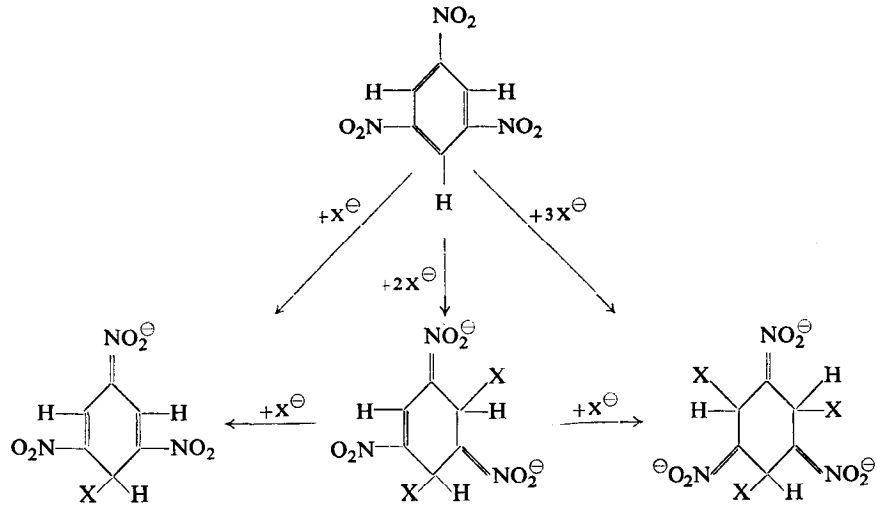
Aromatic hydroxylation is known to take place in animal and human organisms and therefore it is of great importance to know the metabolism of various aromatic compounds including drugs (D. Robinson, J. N. Smith, R.T. Williams [47]). The presence of the nitro group in a molecule, resulting in its activation, may sometimes lead to a rather unusual course of reaction. The Richter [48] reaction might be taken as an example, in which *m*- bromobenzoic acid may be obtained by reacting potassium cyanide with *p*- nitrobromobenzene. Likewise, when reacting potassium cyanide with *m*- nitrobromobenzene, a mixture of *o*- and *p*- bromobenzoic acids are formed.

According to Bunnett and his co-workers [49,50,50a] the reaction is of the nucleophilic substitution type and may be represented by the following scheme:

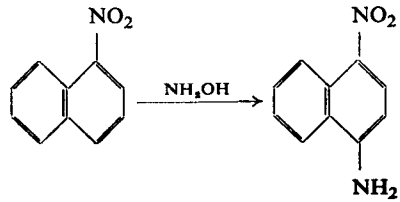


(26)

Holleck and Perret [51] gave the following diagrammatic presentation of nucleophilic addition of the OH^- or CN^- ion to *sym*- trinitrobenzene in alkaline medium ($X=OH^-$ or CN^-):

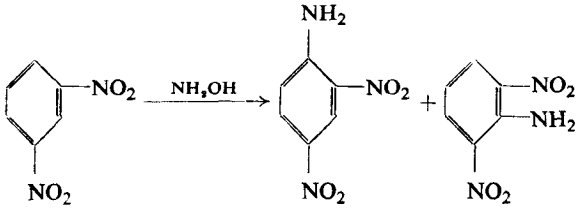


According to Angeli and Angelico [52], and later Meisenheimer [38], aromatic nitro compounds react with hydroxylamine to form aminonitro derivatives. Thus, Angeli obtained 1-nitro-4-naphthylamine from 1-nitronaphthalene:

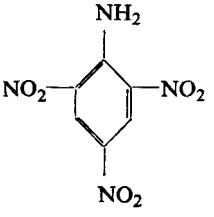


(27)

In the case of nitro derivatives of benzene at least two nitro groups should be present on the ring. Here are the most typical reactions, as suggested by Meisenheimer :



(28)



(28a)

Here the ammo group enters the *ortho* or *para* position in relation to the nitro groups.

The reaction of sulphitation of polynitro compounds is also a nucleophilic substitution reaction. It is dealt with more fully on pp. 237, 308 and 332.

The so-called Janovsky reaction [53] is a very characteristic one for many higher nitrated benzene derivatives. It is probably also of nucleophilic character. It consists in treating a diluted di- or tri-nitro compound solution in acetone with a concentrated solution of potassium or sodium hydroxide (generally of 30% concentration). The acetone solution turns bright coloured. Red to violet colours may appear according to the nitro compound present.

Thus, as Janovsky [53] reports, *m*- dinitrobenzene produces a reddish violet colour, 2,4-dinitrotoluene a blue one, 1,3-dinitronaphthalene a bluish-red.

Bitt6 [54] stated that di- and tri-nitro compounds give colour reactions with a number of aliphatic and aromatic aldehydes and ketones in the presence of alkalis.

Thus, *m*- dinitrobenzene produces the following colours:

with pulegone	hyacinth red
with carvone	blue pink
with camphor (in nitrobenzene solution)	brown red
with propionic aldehyde	dark brown

No colour appears with some aldehydes, for example, furfural and cinnamic aldehyde. Bittó has suggested this reaction may be used for the identification of aldehydes and ketones (see also p. 239).

The Janovsky reaction and its Bittó modification were investigated by Reitzenstein and Stamm [55]. Both these as well as other authors (Bost and Nicholson [56], Nisida [57], Canäck [58]) stated a number of irregularities.

Thus, nitro compounds with a great number substituents, for example trinitromesitylene, do not give any colour reactions. Compounds with nitro groups located in the 2,4-positions, produce colours that depend to a considerable extent on the substituent in position 1. The presence of the OH or NH_2 group interferes with the colour reaction. The situation remains unchanged after both of the groups have been acylated, while alkylation of a phenol restores the ability to produce colour.

Newlands and F. Wild [59], when investigating maxima of the absorption spectra of coloured solution, obtained with various dinitro compounds, found that some of them produce two maxima.

T. Urbanski, Kwiatkowska and Kutkiewicz [60] came to similar conclusions. Table 26 lists some of the results obtained.

TABLE 26

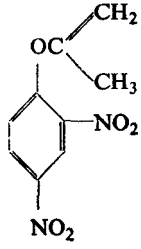
ABSORPTION SPECTRA OF COLOURED COMPOUNDS PRODUCED BY THE JANOVSKY REACTION

Compound	Colour	Absorption maxima mμ	Reference
m- Dinitrobenzene	violet	570-573	[60]
o- Dinitrobenzene	none		[60]
p- Dinitrobenzene	none		[60]
2,4-Dinitrotoluene	bluish-violet	570-575	[60]
3,5-Dinitrotoluene	reddish-violet	450-460 and 575	[60]
1,3,5-Trinitrobenzene	reddish-violet	562 and 573	[60]
1,2,3-Trinitrobenzene	reddish-violet	562	[60]
1,2,4-Trinitrobenzene	red	525	[60]
2,4,6-Trinitrotoluene	blood red	460 and 540	[60]
2,3,4-Trinitrotoluene	violet	550	[60]
2,4,5-Trinitrotoluene	yellow-green	425-430 and 630	[60]
1-Fluoro-2,4-dinitrobenzene	greenish-blue	430 and 550	[59]
1,3-Dichloro-4,6-dinitrobenzene	deep blue	640	[59]
2,4-Dinitrophenetole	reddish-violet	560	[59]
2,4-Dinitroaniline	red	560	[59]
2,4-Dinitrophenylamine	red	590	[59]
2,4-Dinitrophenylhydrazine	blood red	570	[59]

Abe [61] investigated the rate of the colour development with *m*- dinitrobenzene in acetone in the presence of sodium hydroxide by examining the intensity of the band 560 mμ against time. The maximum intensity occurs after 9 min. The more concentrated the solution of sodium hydroxide the more quickly the colour fades.

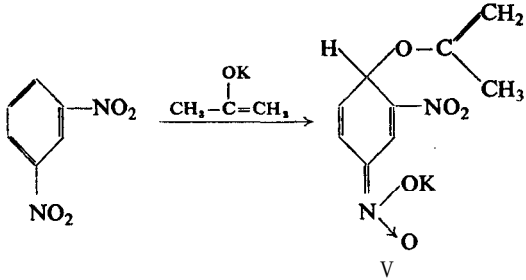
According to Cone [62] it is advisable to use butanone (methyl ethyl ketone) instead of acetone, because the former gives a more stable colour and the reaction can be used for colorimetric determination of TNT in air.

The nature of the Janovsky's colour reaction is not sufficiently understood. Reitzenstein and Stamm [55] were the first to try to establish the structure of the compounds formed. They were able to isolate from an acetone solution a brown product (IV), resulting from the reaction of 1,2,4-chlorodinitrobenzene with the enolic form of acetone:



IV

Quite recently Gitis [42] isolated a number of coloured products formed by polynitro compounds with acetone in the presence of sodium hydroxide. The author, like Reitzenstein and Stamm, postulated that it was the enol form of acetone that reacted with a nitro compound, products of nucleophilic substitution of the type described by Meisenheimer [36-38] (p. 202), being formed:



(29)

V

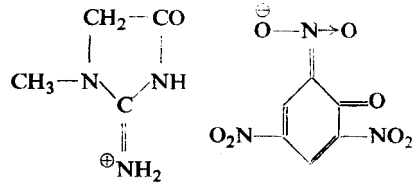
Gitis believes that compounds of the V type are the main products of the Janovsky reaction.

The formula V is not in agreement with the views expressed by various authors on the structure of the coloured products obtained by adding substances containing an active methylene group to higher nitrated aromatic compounds, starting from *m*- dinitrobenzene. A number of papers have been published on the subject. They ori - ginated from the Jaffe-Folin [63,64] reaction for quantitative calorimetric determination of creatinine. The reaction consists in the development of a red colour when solutions containing creatinine are treated with aqueous picric acid and a few drops of alkali at room temperature. Many (but not all) compounds with active CH_2 group are capable of giving this reaction.

Several red compounds have been isolated from the red solution obtained from creatinine, picric acid and alkali. By acidification a red powder was isolated by Greenwald and Gross [65]. On boiling with water (Anslow and King [66]) or on heating to 139°C this was transformed into the usual yellow creatinine picrate.

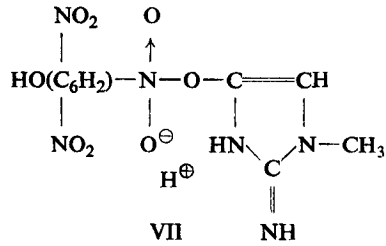
It was considered originally to be a tautomer of the picrate. More recently, by treating aqueous solutions of creatinine picrate of different compositions with alcohol, several crystalline compounds have been obtained (Bollinger [67]).

The formula VI was originally suggested for the red tautomer of creatinine picrate



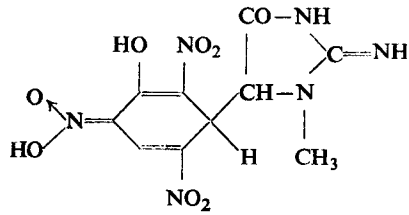
VI

Because non-basic substances may also produce a similar reaction, it was later suggested by Anslow and King [66] that the enolate anion of creatinine forms a coordinate bond with the positively charged nitrogen atom of one of the nitro groups. The structure of the compound they postulated is VII:



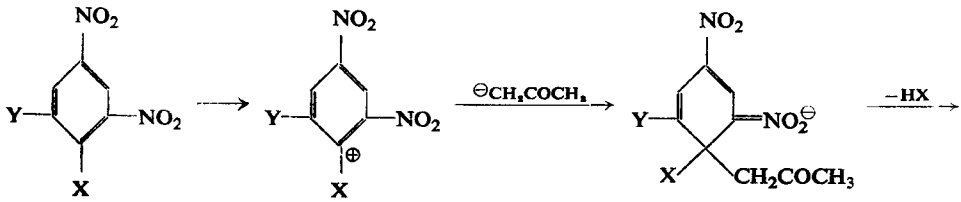
VII

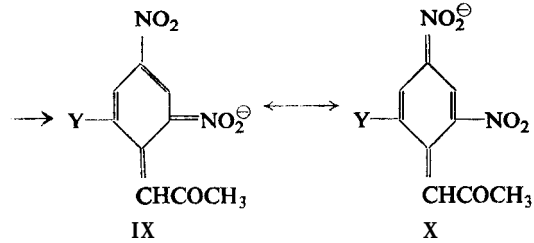
According to the most recent suggestion (Kimura [69]), the product of the reaction of picric acid with creatinine is not a substitution but an addition product VIII:



VIII

With regard to the other coloured compounds formed from *m*- dinitrobenzene or *sym*- trinitrobenzene, it was claimed that the carbanion of active methylene compounds condenses with the nitro compound in terms of nucleophilic substitution :





(30)

X = H, OH, Cl
Y = H, NO_2

This mechanism was suggested by Ishidata and Sagakuchi [68].

The formula X may be considered to correspond with the coloured products of the Janovsky reaction.

Recently T. Urbanski [70] established that an alcoholic solution of *m*- dinitrobenzene is coloured pink with primary nitroparaffins in the presence of sodium hydroxide. The colour is very intense when nitromethane is used. The spectrum of the solution shows a maximum of absorption near 550 mμ.

The formation of the coloured products is most likely due to the presence of the active methylene group in the primary nitroparaffins. Secondary nitroparaffins do not give this reaction.

The reaction can be used to detect the presence of nitromethane (T. Urbanski and Kwiatkowska [70a].

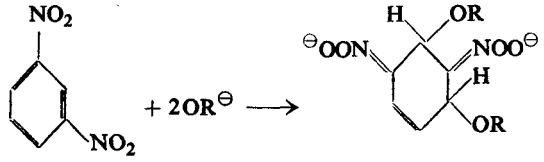
2,4-Dinitrotoluene does not give this reaction. Trinitro compounds (such as *sym*-trinitrobenzene and α– trinitrotoluene) also give the colour reaction but this is less typical, as the trinitro compounds give a similar colour with alcoholic NaOH alone without primary nitroparaffins.

The reaction of nucleophilic substitution described above admit the ease of formation of quinoid ring. The problem of quinoid ring formation was recently examined by Perret and Holleck [47]. On the basis of their spectroscopic ultraviolet investigations using visible and infra-red techniques and their polarographic investigations, Perret and Holleck came to the conclusion that differently substituted derivatives of *sym*- trinitrobenzene possess different abilities to form a quinoid structure. Trinitrotoluene belongs to those derivatives which behave in a polarograph in much the same manner as *sym*- trinitrobenzene because the methyl group does not take part in the formation of quinoid structure. On the contrary OH groups promote the formation of quinoid structures.

The ability of higher nitrated aromatic compounds to form dark coloured products in alkaline medium can be used for the titration of certain weak acids with bases. For example trinitrobenxene acquires an orange and red colour at pH 12.2 and 13.6 respectively.

The formation of coloured compounds was used by Brockmann and Meyer [71] for the quantitative determination of polynitro compounds. The di- or trinitro compound is dissolved in ethylenediamine and titrated potentiometricallv

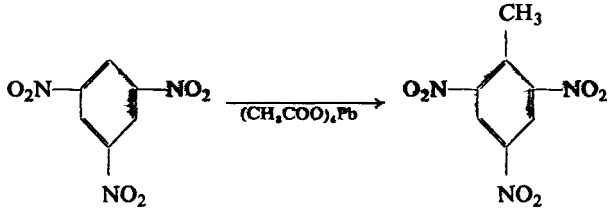
with an 0.1 N solution of sodium colamate. The nitro compound behaves as a Lewis acid:



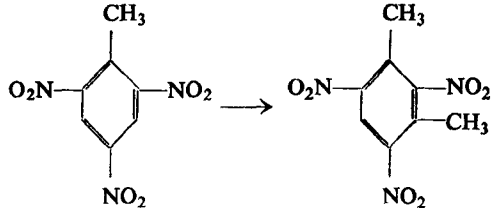
m- Dinitrobenzene and α– trinitrotoluene require two and three equivalents of colamate respectively. On reaction of polynitrocompounds with diazomethane- see [160].

FREE RADICAL REACTIONS

Nitro groups also enable free radical reactions to occur with aromatic rings. As Fieser's investigations [71a] have shown, aromatic nitro compounds can be methylated when reacted with lead tetraacetate:



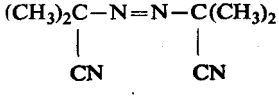
(31)



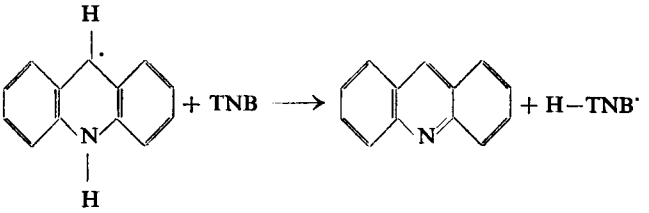
(32)

The reactions probably involve free radicals. The lead tetraacetate liberates the methyl radical, which reacts with the aromatic free radical.

It is characteristic that the new entrant methyl group assumes the ortho position to the nitro group and thus a substitution occurs which is similar to nucleophilic attack. Recently it has been found by Jackson and Waters [72] that higher nitrated benzene derivatives such as *m*- dinitrobenzene, or 1,3,5-trinitrobenzene, become homolytic hydrogen acceptors at temperatures of 80-100°C especially in the presence of the 2-cyano-2-propyl radical, which is formed by thermal decomposition of a,a'-azo-bis-isobutyronitrile



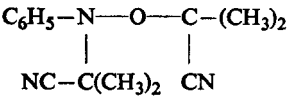
Owing to this, an acrydane, for example, can be converted under the influence of *m*- dinitrobenzene or 1,3,5-trinitrobenzene into acridine in the presence of the above mentioned radical :



(33)

In the presence of 2-cyano-2-propyl, using 0.72 mole of trinitrobenzene, actidine can be obtained in 64% yield, whereas without the radical the yield is only 4%.

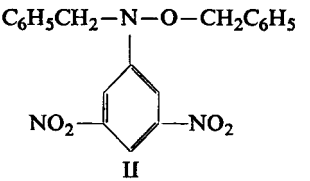
This reaction suggests that free radicals may act as reducing agents (Haines and Waters [73]). Indeed, Inamoto and Simamura [74] have recently proved that the 2-cyano-2-propyl radical can react with nitrobenzene to give small quantities of O,N-di(2-cyano-2-propyl)-N-phenylhydroxylamine (I).



I

Thus it has been found that the free radical attacks the nitro group resulting in its partial reduction. Apart from this acetone is also formed.

Jackson, Waters and Watson [75] found that the free benzyl radical (prepared by the method reported by Beckwith and Waters [76] in 1957, which consists in heating dibutylperoxide with toluene to the boiling point of the latter under a nitrogen atmosphere) reacts with 1,3,5-trinitrobenzene, to form O,N-dibenzyl-3,5-dinitrophenylhydroxylamine (II) in 28% yield. In addition to this, benzaldehyde was formed though it was never produced in the absence of trinitrobenzene.



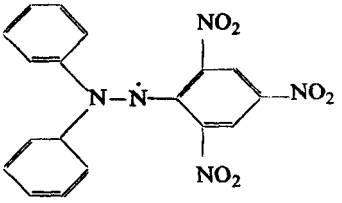
II

The overall equation is:

$$C_6H_3(NO_2)_3 + 4C_6H_5CH_2^* \rightarrow II + C_6H_5CHO + C_6H_5CH_3 \qquad (34)$$

It follows from the above equation that one nitro group destroys four free radicals. A further conclusion is that the complete reduction of a nitro group to an amino group would destroy six free radicals.

Recently Eley and Parfitt [77] discovered that a,a'-diphenyl- β -picrylhydrazyl (DPPH) (III) is one of the best organic semiconductors with an energy gap of only 0.26 eV.



III

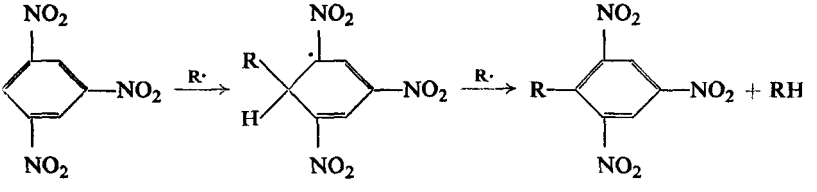
The mobile electron is most likely that associated with the free valency on the N atom.

INHIBITING ACTION OF NITRO COMPOUNDS ON POLYMERIZATION

Another example of the homolytic reaction of nitro compounds with free radicals is their inhibiting effect on addition polymerization of vinyl compounds, especially by the higher nitrated compounds which have the most pronounced inhibiting properties.

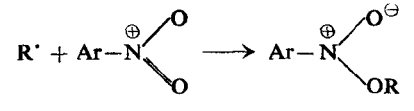
This property of nitro compounds was first observed by Foord [78] with regard to *o*- nitrophenol, 2,4-dinitrophenol, picric acid, *m*- dinitrobenzene, 2,4-dinitrotoluene, 1,3,8-trinitronaphthalene, 2,4-dinitroaniline and other higher nitrated aromatic compounds.

Subsequently Price and Durham [79] stated their view regarding the inhibition of polymerization, which, according to them, consisted in a free radical reaction, analogous to the reaction of alkylation of trinitrobenzene, discovered by Fieser and his co-workers [71a], which has already been described. Price [80] suggested the following mechanism for the reaction, assuming that two molecules I and II were formed from a polymerizable radical k:

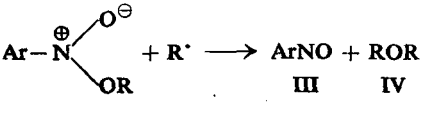


I II

However, Bartlett and his co-workers [81,82] provided evidence, based on the study of the reaction kinetics, which proved that inhibition of polymerization started at the oxygen atom of a nitro group:



(35a)



III IV

(35b)

Stopping the polymerization consisted here in the formation of a nitro compound (I) and an ether (IV).

Bartlett and Kwart [81] gave the figures referring to the so-called inhibition constants in the polymerization of vinyl acetate under influence of various substances, and mainly nitro compounds (Table 27).

TABLE 27

INHIBITION CONSTANTS IN THE POLYMERIZATION OF VINYL ACETATE AT 45°C

Inhibitor	Z_1 (initial inhibition constant)
Nitrobenzene	38
p- Nitrotoluene	40
Dinitrodurene	2.5
o- Dinitrobenzene	96
m- Dinitrobenzene	105
p- Dinitrobenzene	267
sym-Trinitrobenzene	890
Sulphur	410

More recent investigations by Ihrig and Wong [83] in which the authors used optically active nitrodiphenyl derivatives for studying the mechanism of the reaction, confirmed the second scheme, i.e. the attack on a growing radical by a nitro group.

Recently Inamoto and Simamura [74] investigated the interaction of l-cyano-1-methylethyl radicals and various nitro compounds (nitrobenzene, *m*- dinitrobenzene, nitromethane, tetranitromethane) and Bevington and Ghanem [84] have studied the effects of picric acid and *m*- dinitrobenzene on the sensitized radical polymerization of styrene. Picric acid proved to be a rather inefficient inhibitor. *m*- dinitrobenzene was found to be a polymerization retardant. By using ^{14}C-labelled specimens of the nitro compounds the authors determined the amounts of nitro compounds incorporated in the polymer. The average number of retardant molecules per polymer molecule was found to be 0.5-0.7.

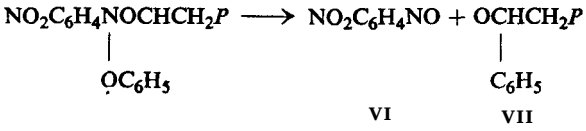
On the basis of these experiments and of those of Inamoto and Sinamura, Bevington and Ghanem suggest the interaction of polymer radical with *m*- dinitrobenzene is likely to be:

$$C_6H_4(NO_2)_2 + PCH_2\underset{\displaystyle C_6H_5}{\underset{|}{C}}H^{\cdot} \longrightarrow NO_2C_6H_4N\overset{\displaystyle \dot{O}C_6H_5}{\overset{|}{O}}CHCH_2P \qquad \text{(36a)}$$

V

where *P* represents a polystyrene chain with a terminal initiator fragment.

The next stage would be the formation of the nitroso compound:



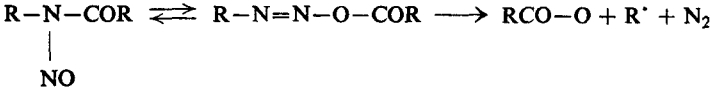
(36b)

Next, various interactions between V, VI, VII and free radicals would occur.

As Kite [85] observed, aromatic nitro compounds inhibited the polymerization of vinyl acetate more strongly than that of methyl methacrylate.

It is interesting to see, that C-nitroso- and N-nitroso compounds (e.g. nitroso-acetanilide, N-nitrosoacylarylamines) catalyse polymerization reactions (Hey [86-88], Blomquist, Johnson and Sykes [89]).

Hey suggested in 1947 the following plausible scheme for the action of N-nitroso-acylarylamine :



(37)

This action is similar to that of benzoyl peroxide.

VULCANIZATION OF RUBBER WITH AROMATIC NITRO COMPOUNDS

Ostromyslensky [90] observed that rubber could be vulcanized in the absence of sulphur or its compounds if small quantities of aromatic nitro compounds, e.g. nitrobenzene, dinitro- or *sym*- trinitro-benzene, tetranitronaphthalene plus certain oxidizing compounds, such as benzoyl peroxide, were added to it. The resultant vulcanized rubber had mechanical properties not inferior to those of a product vulcanized by sulphur alone, and when free from accelerators it exhibited a greater resistance to ageing. Some metal oxides, such as PbO, CaO, BaO, promoted vulcanization by nitro compounds. Urea played the role of an accelerator of vulcanization. These observations have been confirmed in more recent studies by other workers.

The action of *m*- dinitrobenzene chiefly as a vulcanizing agent, has been studied by Wright [91] and Blake [92] who found that all the *m*- dinitrobenzene entered into reaction with rubber when added in the proportion of 6%. Blake failed to obtain hard rubber ("ebonite") that way. A method for obtaining hard rubber by using *m*- dinitrobenzene was, however, described by Wright [91]. Rubber vulcanized by nitro compounds has the advantage of not corroding metals (Koshelev [93]).

The investigation of sulphurless vulcanizing agents, including the use of polynitro derivatives of benzene, has been completed by Mark and his co-workers [94]).

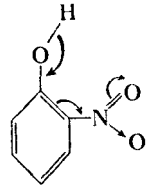
The hypothesis has been advanced that during the vulcanization of natural rubber by means of polynitro compounds, a partial reduction of polynitro- to nitroso compounds takes place, the latter being known as vulcanizing agents.

In practice, the application of nitro compounds (e.g. *m*- or *p*- dinitrobenzene)

in the vulcanization of rubber is limited to butyl rubber, as may be seen from the patent literature [94a].

INFLUENCE OF NITRO GROUPS ON SOME PHYSICO-CHEMICAL PROPERTIES OF PHENOLS AND AMINES

The nitro group enhances the acidic properties of phenols, possibly due to the influence of the induction effect (p. 197):



The comparison of dissociation constants (K) of several phenols in aqueous solution with those of their nitro derivatives (Table 28) illustrates this effect of the nitro group.

TABLE 28

Phenol	K	Reference
Phenol	1.2×10^{-10}	[82]
o- Nitrophenol	6.8×10^{-8}	[82]
m- Nitropheno1	5×10^{-9}	[82]
p- Nitrophenol	7×10^{-8}	[82]
2,4-Dinitrophenol	5.6×10^{-4}	[83]
2,6-Dinitrophenol	1×10^{-4}	[84]
Catechol	3.5×10^{-10}	[82]
3-Nitrocatechol	1.88×10^{-6}	[84]
Hydroquinone	4.5×10^{-11}	[82]
Nitrohydroquinone	1.01×10^{-6}	[84]

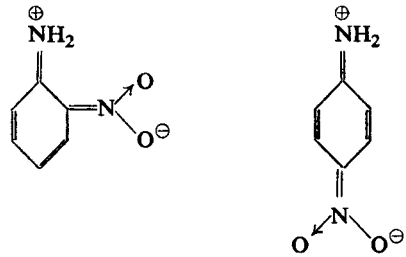
A nitro group ortho to the phenol group can form a chelate through an internal hydrogen bond (p. 177, see also p. 171).

This structure accounts for certain properties of *o*- nitrophenol, and namely those by which it differs from its ***m***- and *p*- isomers. For example, *o*- nitrophenol is volatile in steam. This may be explained by the fact that owing to the presence of an internal hydrogen bond, the intermolecular links which are responsible for molecular association are either weakened or non-existent. This is the reason why the

phenolic group in *o*- nitrophenol is not capable of molecular association, unlike *m*- and *p*- nitrophenols.

The nitro group also strongly influences the amino group present in the ring, reducing its basic properties. This influence is strongest when it is in the *ortho* or *para* position to the amino group. The reactivity of the amino group is so enhanced that *o*- or *p*- nitroaniline, when boiled in a aqueous solution of sodium hydroxide, are hydrolysed to form *o*- or *p*- nitrophenol. *m*- Nitroaniline is not subject to this reaction.

This specific property of *o*- and *p*- nitroaniline may be explained by assuming the structure of an amphoteric ion:



I II

However, this formula for *m*- nitroaniline cannot be accepted as it requires the assumption of the *m*- quinone structure which is unknown at present.

To confirm the formula II, reference is made to the fact that the dipole moment of *p*- nitroaniline ($\mu = 6.45$) is much higher than that which would be deduced from the total of the dipole moments of aniline ($\mu = 1.52$) and nitrobenzene ($\mu = 3.96$).

The nitro group may, in some cases, form a hydrogen bond with a primary or secondary amine group in the ***ortho*** position to the nitro group. Thus, Hathway and Flett [98], on the basis of their investigations of the infra-red absorption spectra of 1,2- and 2,1-nitronaphthylamines, inferred that such a bond might exist.

However, more recent studies by Dyall and Hambly [99] as well as by T. Urbanski and Dabrowska [100] with nitro derivatives of aniline have shown that in *o*- nitroaniline such a bond cannot be confirmed so that for the time being we can go no farther than speaking of an ion bond.

BEHAVIOUR OF NITRO COMPOUNDS IN CONCENTRATED ACIDS

As stated by Hantzsch [101] on the basis of cryometric measurements, the nitro group itself could be of a basic character. The author had studied the behaviour of nitromethane, *p*- nitrotoluene, *m*- dinitrobenzene and 2,4,6-trinitrotoluene in oleum solutions. Among all the compounds investigated, only *p*- nitrotoluene be-

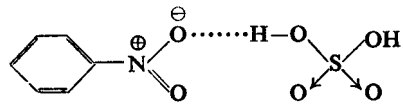
haved abnormally, as its molecular weight increased with the increase of the concentration of solution. Hantzsch suggested that an addition compound, ($ArNO_2$. .H_2SO_4), was formed by adding a sulphuric acid molecule on to the nitro group, as if it had a basic character.

The investigations were continued by Hammett [102] and by Gillespie [103, 103a]. This work established that if oleum of high concentration was used as a solvent, higher nitrated aromatic compounds also exhibited basic properties.

These results were not quite in agreement with those of spectrophotometric investigations reported by Brand and his co-workers [104]. Brand suggested that the difference was due to insufficient knowledge of the true form of nitro compounds in the solutions under consideration. He assumed that nitro compounds in sulphuric acid solutions became cations (Ar-$\overset{\oplus}{N}\overset{O}{\underset{OH}{\nearrow\searrow}}$). That was in agreement with an earlier hypothesis (Masson [105], Hetherington and Masson [106]) on the mechanism of aromatic nitration.

In support of Hantzsch's view reference should be made to the fact that Metro compounds can form addition products with sulphuric acid. Thus, Cherbuliez [107] isolated $C_6H_5NO_2.H_2SO_4$ (m. p. 11.6°C) as the product of addition of nitrobenzene to sulphuric acid. This was later supported by Masson [105] who assigned a salt structure to the product $[C_6H_5NO_2H^+]$ $[HSO_4^-]$.

Gillespie and Millen [108] assumed that in such a substance both molecules were linked by a hydrogen bond:

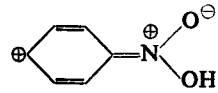


Confirmation of that view has been provided by Hammett and Chapman's work [109]. They inferred from their examination of the solubilities of various organic compounds, among others nitrobenzene, in mixtures of sulphuric acid and water that this form of hydrogen bonding could exist. It might be that similar hydrogen bonds were also formed between *m*- dinitro- or *sym*- trinitro-benzene and sulphuric acid. Gillespie and Millen [108] had drawn attention to that, basing their supposition on the observation by Klough, Savage and van Marl [110], that the solubilities of higher nitro compounds increased rapidly with increase in the concentration of sulphuric acid.

Also Hammond and Medic [111] on the basis of analysis of the ultra-violet spectrum, advanced the hypothesis that sulphuric acid combined with the nitro group through a hydrogen bond. Liler and Kosanovic [150] came to the same conclusion on the basis of their experiments on viscosities, electrical conductivities and refractivities of solution of nitro compounds in sulphuric acid.

On the other hand it should be emphasized that solutions of aromatic nitro compounds, especially mononitro derivatives are distinctly coloured, as already observed by Hantzsch [101]. The yellowish colour of nitrobenzene and *p*- nitro-

toluene becomes more intense under the influence of sulphuric acid. That is ascribed to the formation of the quinonoid ion:



in the protonizing medium of sulphuric acid.

ADDITION COMPOUNDS OF AROMATIC POLYNITRO COMPOUNDS

The ability to form addition compounds, especially with aromatic hydrocarbons composed of condensed rings, is one of the specific properties of aromatic polynitro compounds. For example, compounds of trinitrobenzene or picric acid with naphthalene, as well as with other hydrocarbons with condensed rings, are very characteristic. Generally they are intensely coloured.

The nature of the bonds forming molecular addition compounds has been investigated by several workers, but up to now it has not been made sufficiently clear. Pfeiffer [112] held that complex formation was due to the mutual saturation of "residual valencies", but Briegleb [113,114] advanced the theory that addition compounds should be regarded as "polarization aggregates" which owed their stability to electrostatic interactions, possibly due to polarization of one component by the other. Thus, in the case of polynitro compounds, their strongly polar mole cules influence the non polar molecules of the hydrocarbon. Further, no covalent bonds exist between these two kinds of molecules. This hypothesis has received considerable support and a new development.

The experimental observations which support this point of view are as follows:

(1) The interatomic distances between the two components were found by X-ray analysis to be of the order 3.0-3.5 Å (Powell and Huse [115]; Rapson, Saunder and Stewart [116]). This is too long for covalent bonds.

(2) Molecules of 1,3,5-trinitrobcnzene or *p*- dinitrobenzene have no electric dipole moments but they have moments in solutions where molecular compounds are formed. For example they have no moments in carbon tetrachloride or chloroform, but they do have moments in benzene, naphthalene, or dioxane.

(3) Molecular addition compounds are readily formed and decomposed, e.g. by acting with a suitable solvent, which would dissolve one of the components and extract it. For example addition compound formed between picric acid and a hydrocarbon can be split into its components by extracting the picric acid with alcohol while the hydrocarbon remains undissolved. Another fact also indicative of the instability of the addition products is that those of picric acid may be decomposed by treating their solutions with saturated solution of potassium chloride. Potassium picrate is then precipitated, while the other component remains in solution (Taben and Kosak [117]). Generally speaking, the organic addition compounds

are dissolved in solution to a considerable extent. All this would be impossible if they were formed by covalent bonds.

(4) Measurable, although small, conductivities have been observed for some molecular addition compounds (picric acid-naphthalene and 1,3,5-trinitrobenzene--naphthalene) in liquid sulphur dioxide, according to Weiss [118]. He suggests that the complex molecule is essentially ionic in character, being formed by electron transfer from the hydrocarbon (donor A) to the polynitro compound (acceptor B), according to the diagrammatic reaction ("charge transfer compounds"):

$$A + B \rightleftharpoons A^{\oplus}B^{\ominus}$$

A number of authors have studied the emission spectra characteristics of many complexes of sym-trinitrobenzene (TNB) with aromatics (Reid [119]; Bier and Ketelaar [120]; Bier [121]; Czekalla, Briegleb ***et al.*** [122]; McGlynn and Boggus [123]). These experiments led to the conclusion that in most complexes the emission is a charge transfer (E -> N) emission.

McGlynn and Boggus describe the phenomenon thus: absorption in the charge transfer band is followed either by the converse emission or by intersystem crossing (according to Kasha [124]) to a dissociative level of the complex which yields the aromatic in its first excited triplet state. The aromatic hydrocarbon then phosphoresces.

(5) It is now recognized that electron transfer from one component to another is responsible for the change of colour noticed in some molecular compounds (cf. Orgel [125]).

Brackman [126] showed that it was possible to arrange the components of the molecular compounds in such a way that if the colours of the molecular compounds were plotted against the nitro compound, a series of roughly parallel straight lines was obtained (Fig. 47†). It will be noted that an increase in the number or power of the electron-attracting groups in the nitrobenzene nucleus produces a bathochromic effect (a shift towards longer waves), while an increase in the number of electron-repelling groups has the opposite effect (hypsochromic effect).

(6) The magnetic susceptibility of some addition compounds, such as naphthalene picrate, is nearly additive, i.e. equal to the sum of the components (Le Fèvre [127], Baddar and Mikhail [128]). This would suggest that the molecules are held by weak electrostatic forces.

(7) The ultra-violet absorption spectra of the addition compounds have been found to be additive, i.e. equal to the sum of the spectra of components, according to Friedel and Orchin [129]. This would also support the theory of ionic bond between the components.

(8) The stability of an addition compound ($A^{+}B^{-}$) is affected by the Presence of strong donor and acceptor groups. Thus electron-donor groups in molecule A and/or electron-acceptor groups in B lead to a greater binding energy be-

† Here not only aromatic nitro compounds are given, but also aliphatic such as nitromethane, tetranitromethane and also chloranil, benzoquinone, maleic and phthalic anhydrides.

tween A and B (Buehler *et al.* [130]). This would explain the superiority of trinitrobenzene over picric acid as a complex forming agent.

(9) The heat of formation in solution of the addition compound of picric acid and naphthalene determined by Brönsted [131], using e.m.f. measurements, was found to be 2.15 kcal/mole. Similar figures were obtained by cryometric measure

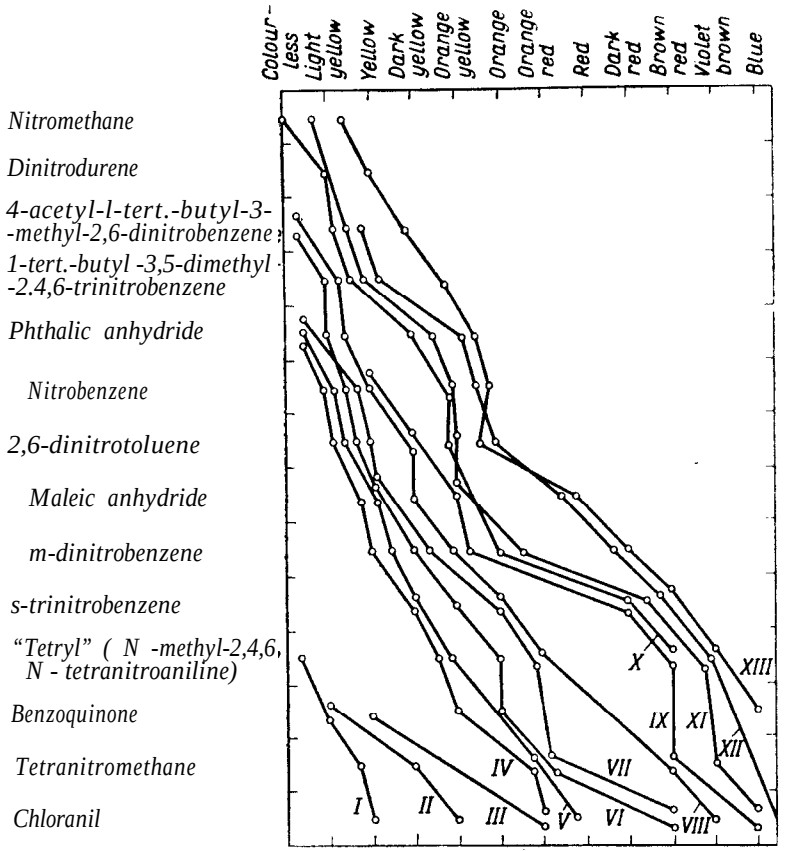


FIG. 47. Colours of addition products of various nitro compounds with hydrocarbons and amines: I - Benzene; II - Xylene; III - Durene; IV - Naphthalene; V - Acetanilide; VI - Phenanthrene;VII - Tribromoaniline; VIII - Safrole; IX - Anthracene; X - Aniline; XI - Diphenylamine; XII - Benzidine: XIII -Dimethylaniline (Brackman [126]).

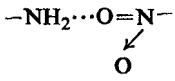
ments (Brown [132]), and solubility measurements (Moore, Shepherd, Goodall [133]). However, all these measurements have neglected the heat of solution. Briegleb [114] applied another method which gave more exact figures. He took advantage of the fact that most of the addition compounds were strongly coloured and measured the colour change of the solutions with temperature. He found that the heats of formation of compounds of 1,3,5-trinitrobenzene with various hydrocarbons in carbon tetrachloride varied between 1.5 and 4.5 kcal/mol.

He also studied the effect of the solvent and found that it should not be neglected :

	Heats of formation	
	in $CC1_4$	in $C_2H_2Cl_4$
anthracene-m-dinitrobenzene	2.2 kcal/mole	1.5 kcal/mole
anthracene-sym-trinitrobenzene	4.4 kcal/mole	3.6 kcal/mole

Ross and Labes [I34] determined the heats of formation of the addition compounds: 1,3,5-trinitrobenzene-naphthalene and -aniline, and found them to be 3.3 and 5.1 kcal/mole respectively.

According to Kross and Fassel [135], addition compounds between nitro compounds and amines can be formed through hydrogen bonds of the type:



This was based on the shift in frequency of the nitro group bands in the infrared absorption spectrum.

It has also been suggested that 1,3,5-trinitrobenzene and *m*- dinitrobenzene may react with amines to form addition compounds by a proton transfer reaction (Lewis and Seaborg [136], Farr, Bard, and Wheland [137]).

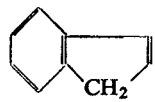
However, Field, W. G. Garner and Smith [138] had concluded earlier that proton transfers do not occur in liquid ammonia solutions of *m*- dinitrobenzene. On the basis of ultra-violet and visible absorption spectra and electrical conductance measurements of the products of interaction of polynitroaromatic compounds with a variety of amines, Miller and Wynne-Jones [139] came to the conclusion that:

(a) Proton transfers do not appear to be involved in the formation of complexes by 1,3,5-trinitrobenzene but electron transfers probably occur.

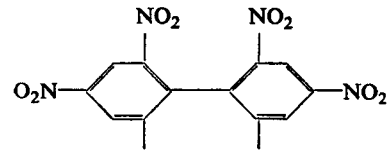
(b) Both proton transfers and electron transfers occur when 2,4,6-trinitrotoluene and 2,4,6-trinitro-m-xylene react with amines.

Steric factors in addition compounds also ought to be referred to when considering formation of addition compounds. X-ray diffraction studies (e.g. Powell and Huse [115], Rapson, Saunder and Stewart [116]) have shown that in general the crystalline addition compounds consist of alternate layers of the two components. The approach of the acceptor molecule can be sterically hindered if the donor molecule is non-planar. Hence complex formation is difficult as the non-planarity increases the distance between the components. For example, trans-stilbene forms a picrate, but the cis-isomer does not. The planar molecule of 2-phenylnaphthalene also forms a picrate, while its non-planar isomer, 1-phenylnaphthalene, fails to do so.

Hammick and Sixsmith [140] found that indene (X) and dimethyl-4,6,4',6'-tetranitrodiphenate (XI) formed an addition compound at a relatively low rate, which could be measured.



X



XI

This means that steric barriers exist which must be overcome to form an addition compound owing to nonplanarity of the nitro compound. The steric factor could also explain the fact that the addition compound reacts only slowly with bromine, whereas indene itself rapidly adds bromine to form a dibromide.

A detailed list of addition compounds formed by *sym*- trinitrobenzene, 2,4,6-trinitrotoluene, picric acid and other polynitro compounds is given in the appropriate paragraphs devoted to these nitro compounds.

It is important to add that some molecular addition compounds of *sym*- trinitrobenzene with hydrocarbons can serve for identification and purification of hydrocarbons (Veibel [141]). Trinitrofluorenone seems to be of particular value (Orchin and Woolfolk [142], Lepley [154]).

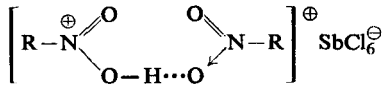
As shown by T. Urbanski [143] between 1933 and 1937, there is a group of molecular addition compounds whose existence cannot be explained by all the points mentioned above. They are addition compounds of certain nitro compounds with esters of nitric acid. Thus many aromatic mononitro compounds form addition compounds with mannitol hexanitrate, and some aromatic trinitro compounds do so with erythritol tetranitrate (Vol. II). On the basis of these facts the author suggests that two main reasons are responsible for the formation of these addition compounds :

(1) Assembly of a great number of nitro groups in both components: nitric ester and nitro compound. Incidentally the sum of these groups is eight in the above mentioned examples.

As shown by Hackel [144] glycerine trinitrate (nitroglycerine) does not form addition compounds with any of the aromatic nitro derivatives (mono-, di- or tri-nitro compounds). This is probably due to the inadequate number of nitro groups in nitroglycerine.

(2) The polarity of nitric ester. All esters forming addition compounds possess high polarity. On the contrary, the ester of low polarity-penthaerythritol tetranitrate does not give addition compounds with any of the above mentioned aromatic nitro derivatives.

Complex compounds between nitro compounds and $SbCl_5$ and HCl possess a quite different and clearly ionic character (Klages, Mühlbauer and Uhl [145]). They are stable below 0°C and at 0°C they readily lose HCl. The heat of decomposition (5-6 kcal/mole) suggests that a hydrogen bond is present in the complex to stabilize the salts. The authors suggest the structure



OTHER REACTIONS OF NITRO COMPOUNDS

All aromatic. nitro compounds yield chloropicrin when treated with alkaline solutions of hypochlorous acid salts. The reaction occurs at room temperature or below (the lower the temperature the higher the yields).

The reaction was first observed by Stenhouse [146] in 1847, when treating picric acid with a hypochlorite. According to A. W. Hofmann [147], a 114 wt. % yield could be obtained in the reaction. As Gardner and Fox [148] reported, the yield could be increased up to 180 - 190%. A yield of chloropicrin amounting to about 200% can be obtained by introducing gaseous chlorine into a suspension of sodium picrate in a solution of sodium carbonate at 0°C (Orton and McKie [149]).

It can be assumed that complete transformation of the nitro groups to chloropicrin takes place in the reaction:

$$C_6H_2(NO_2)_3OH + 11Cl_2 + 5H_2O \rightarrow 3CCl_3NO_2 + 13HCl + 3CO_2 \qquad (37)$$

At higher temperatures side reactions occur, among others the formation of nitric acid, while the yield of chloropicrin decreases.

Orton and McKie give the following maximum yields of chloropicrin, obtained from various nitro compounds:

from picric acid	96-97% of the theoretical yield
from 2,4-dinitrophenol	50% " " " "
from *p*- nitrophenol	33-34% " " " "
from *o*- nitrophenol	10% " " " "
from 2,4,6-trinitrotoluene	82-84 wt. %
from 1,3,5-trinitrobenzene	53 " %

For the last two compounds the yields are given in wt. %, since the stoichiometry of the reactions is not known accurately.

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CHAPTER VII

NITRO DERIVATIVES OF BENZENE

ONE or two nitro groups can be introduced by the direct nitration of benzene. The introduction of a third can be accomplished only with great difficulty and the yield obtained is relatively poor. For this reason trinitro derivatives of benzene are prepared by indirect methods. Higher nitrated derivatives of benzene-tetra- and hexanitrobenzene-are also known; they can be obtained by special methods. Dinitrobenzene is the most important of them as an explosive. It was the most used substitute for trinitrotoluene.

NITROBENZENE

PHYSICAL PROPERTIES

Nitrobenzene is a highly toxic, pale, yellow liquid, having a specific smell of bitter almonds. It melts at +5.7°C, and boils at 210.9°C. It was first obtained by Mitscherlich [l] in 1834. The compound is widely used in organic industry as a starting material for the preparation of aniline, benzidine and other intermediates

TABLE 29

SOLUBILITY OF NITROBENZENE IN SULPHURIC ACID ALONE, AND IN THE PRESENCE OF HNO_3, AT 43°C

H_2SO_4 concentration %	$C_6H_5NO_2$ content in the solution, %	Concentration of H_2SO_4, containing 0.2% HNO_3, %	$C_6H_5NO_2$ content in the solution, %
1-6	0.02	-	-
40	0.015		-.
50	0.02	40-50	ca. 0.015
60	0.03	60	ca. 0.02
70	0.04	75	completely soluble
80	completely soluble	-	-

for the manufacture of dyes, medicinals, etc. It is also used for the preparation of dinitrobenzene and as a component of liquid explosives.

The solubility of nitrobenzene in water and in spent nitrating acid is its most important property, which should be borne in mind in its manufacture on account of the possible loss of the product and the toxicity of the waste water.

The relevant data, reported by Groggins [2] are tabulated above (Table 29).

In waste acid of the composition: 0.5% of HNO_3, 74.5% of H_2SO_4, and 25% of H_2O, nitrobenzene dissolves to the extent of 0.03%. The solubility varies little with temperature over the range of 4.4 to 82°C.

The solubility of nitrobenzene in water is given below (Table 30).

TABLE 30

SOLUBILITY OF NITROBENZENE IN WATER

Temperature °C	Quantity of nitrobenzene dissolved, %
4.4	**0.08**
21.1	**0.085**
43.3	**0.090**
71.1	**0.095**

In aqueous solutions of $NaHCO_3$, nitrobenzene dissolves with greater difficulty than in water. The values for 43°C are given below (Table 31):

TABLE 31

SOLUBILITY OF NITROBENZENE IN AQUEOUS SOLUTIONS OF $NaHCO_3$

Concentrations of aqueous solutions of $NaHCO_3$, %	Nitrobenzene dissolved %
1	0.024
3	0.023
7	0.020
10	0.018

The thermochemical properties of nitrobenzene are given on pp. 259-262.

CHEMICAL PROPERTIES

Nitrobenzene is resistant to acids. Bases at certain concentrations and temperatures do not affect nitrobenzene. Only when boiled with NaOH in alcoholic solution, is nitrobenzene reduced to form azoxybenzene. Nitrobenzene does not react with Friedel-Crafts reagents and can be used as solvent in Friedel-Crafts reactions.

The reduction of nitrobenzene may lead to various products, depending on the reaction conditions and on the reducing agent. The subject is dealt with in detail in organic chemistry textbooks.

TOXICITY OF NITROBENZENE

The toxicity of nitrobenzene consists primarily in the formation of methaemoglobine in the blood. It is also toxic for the nervous system and the liver. At concentrations in air exceeding 5 mg/m^3 it is considered dangerous. Poisoning by nitrobenzene may be caused either by its direct contact with the skin or when it is inhaled as vapour. Symptoms of slight poisoning include nausea, headache,

dizziness, and disturbed functioning of the stomach. A blue tinge of the lips and face - cyanosis - is one of the most characteristic symptoms. In acute poisoning, these symptoms are very severe and heart palpitation, loss of consciousness, cramps, and disturbance of vision may also appear. In women it may cause severe menstrual bleeding. The urine of people suffering from nitrobenzene poisoning contains the blood pigment. Chronic poisoning by nitrobenzene may cause anaemia and liver damage.

PREPARATION OF NITROBENZENE

Nitrobenzene is prepared by the nitration of benzene with mixtures of nitric and sulphuric acids of the composition ranging from:

27 to 28% of HNO_3
56 to 58% of H_2SO_4
14 to 17% of H_2O

By the end of the reaction the temperature rises to 70°C.

The quantity of nitrating mixture is calculated with a small excess of HNO_3 (1%), or the nitration is carried out with a volume of mixture insufficient for complete nitration (e.g. 95-97.5%). In the latter case the spent acid does not contain any nitric acid or nitrogen oxides. Nitrobenzene, together with unreacted benzene, is separated from the spent acid. Then benzene is separated from nitrobenzene by distillation. The yield generally amounts to 98% on a large scale, and to about 95% in the laboratory.

At present the nitration of benzene is one of the simplest processes in the organic chemical industry. Nevertheless, the safety factor should not be neglected. The explosion in Rummelsburg of the plant for the nitration of benzene to nitrobenzene, described earlier (p. 152), was the result of defective operation of the nitrator.

The manufacture of nitrobenzene on an industrial scale in the Griesheim (I. G. Farbenindustrie) plant is described below:

2300 kg of benzene is fed to the nitrator and 6500 kg of the nitrating mixture of the composition:

HNO_3	28%
H_2SO_4	58%
H_2O	14%

is added gradually, with vigorous stirring.

At the beginning of acidification a temperature of 25°C should be maintained. During the addition of the first 4000 kg of acid the temperature is allowed to rise up to 35°C. On adding a further 2500 kg of acid the temperature rises up to 60°C. Then the whole is mixed for an hour at 70°C. After cooling, the layer of nitro compound is separated from that of the acid. The spent acid is shaken with benzene to remove any nitrobenzene, nitric acid and nitrogen oxides that may be left. Then the spent acid is transferred to a distillation plant, where it is subjected to concentration up to 70% of H_2SO_4. The benzene from the extraction is either recycled to the nitration plant or is distilled off to separate it from nitrobenzene.

However, the nitrobenzene obtained still contains some acid. To remove it the product is washed with water, then with a 3.0-3.3% solution of sodium hydroxide. The quantity of NaOH used for washing comprises 0.5% of the nitrobenzene weight. In this way not only the remaining acid (which of course is harmless if the nitrobenzene is to be used for further nitration) can be removed, but also any nitrophenols formed in the nitration process. The latter are particularly undesirable impurities in the product. Finally the nitrobenzene is washed once more with water and dried under reduced pressure.

The Leverkusen (I. G. Farbenindustrie) process differs in that it uses a slightly different mixed acid and a rather lower nitration temperature.

The nitrating acid had the composition:

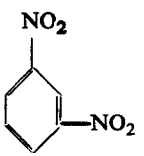
HNO_3	35.5%
H_2SO_4	52.5%
H_2O	12.0%

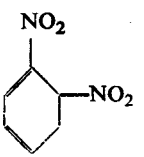
The nitrator (7 m^3 capacity) is fed with 2200 kg of benzene. Mixed acid (4900 kg) is run in for 10 hr, allowing the temperature to rise gradually from 20 to 45°C, which is maintained for further 1 hr with stirring. A sample is taken for a quick test. The density of a crude unwashed sample of nitrobenzene should be 1.200 g/cm^3 at 15°C The waste acid should have the following characteristics: density at 15°C 1.610-1.620 g/cm^3, HNO_3 below 0.2%, HNO_2 below 0.5%. Generally the last two figures are 0.0% and 0.3% respectively.

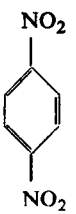
If the test is satisfactory the contents of the nitrator are transferred into another vessel where separation is performed. Three batches are collected in a washing tank, washed with water until neutral to Congo Red and then with water containing ca 0.5% of Na_2CO_3 until strongly alkaline to phenolphthalein. The product is stream distilled until the density of the oil coming over is 1.2. The oil with density < 1.0 is collected and nitrated when a sufficient quantity of it is available for a batch. The oil with a density over 1.0 and below 1.2 is steam distilled with the next batch. The product, freed from unnitrated material, is washed with 3000 l. of water to which 10 kg of a 30% NaOH solution has been added to remove phenols. Then all is washed until neutral and dried at 90°C under reduced pressure. The yield is 98% of the theoretical. The waste acid contains ca. 70% H_2SO_4.

DINITROBENZENES

There are three known isomers of dinitrobenzene - *meta, ortho* and *para:*







PHYSICAL PROPERTIES

The boiling points of the *ortho-*, *meta-*, and *para- isomers* are 319°C, 303°C, and 299°C respectively. The corresponding melting points are 118°C, 91°C and 172°C.

They are all crystalline, pale yellow products, highly toxic, the *ortho-* and *para-*isomers even more than *m-* dinitrobenzene, according to existing data.

Commercial dinitrobenzene is a mixture of the m-dinitro compound, as a principal component, with some 8.0% the *ortho-* and *para-isomers.* It melts at 80-82°C. The melting point of dinitrobenzene for military purposes (as a substitute for TNT) should be 88-89°C.

Dinitrobenzene is of great importance in the organic chemical industry as a raw material for the manufacture of *m-* nitroaniline, *m-* phenylenediamine, sulphur dyes etc.

Dinitrobenzene was used during World War I as a substitute for TNT, since the raw material benzene, necessary for its production, was more readily available than that for trinitrotoluene, and the production process itself was more economical.

Dinitrobenzene was used in Russia (1914-1918) for filling naval mines, in Germany, where it was known as DiFp (Di-Füllpulver), for filling various shells, and in Switzerland.

Even earlier (1879-1880) liquid explosives known as Hellhoffites (Vol. III) had been tried as high explosives. They consisted of nitric acid and dinitrobenzene.

When in the molten state, *m-* dinitrobenzene freezes to form a product having a density of approximately 1.5 g/cm^3. The specific gravity of *m-* dinitrobenzene at different temperatures is given in Table 32 according to Orlova [3]. By compressing powdered *m-* dinitrobenzene, pellets of various densities can be obtained. For example Kast [3a] using pressures of 290 kg/cm^2 and 585 kg/cm^2 obtained products of density 1.29 and 1.44 g/cm^3 respectively.

TABLE 32

SPECIFIC GRAVITY OF *m-* DINITBOBENZENE

Temperature, °C	20	90	120	140	160
Specific gravity	1.577	1.3644	1.3349	1.3149	1.2957

The viscosity [3] of molten m-dinitrobenzene is 0.02528 P at 90°C.

m- Dinitrobenzene is readily soluble in acetone, benzene and toluene and less so in ethyl alcohol. The solubility of the dinitrobenzenes is shown in Table 33, and the solubility of *m-* dinitrobenzene in sulphuric acid in Table 34 [3].

m- Dinitrobenzene forms eutectics with higher nitrated aromatics and with nitric esters. Some of them have been suggested as low melting and low freezing mixtures respectively (Vol. III).

Here are the most important data (Table 35).

TABLE 33
SOLUBILITY OF DINITROBENZENES

Solvent	Temperature °C	100 g of solvent dissolve		
		ortho *g*	*meta* *g*	*Para* *g*
Methanol	20.2	3.3	6.75	0.69
Ethanol	20.5	1.9	3.5	0.40
Propanol	20.0	1.09	2.4	0.30
Carbon disulphide	17.6	0.24	1.35	0.14
Chloroform	17.6	27.1	32.4	1.82
Carbon tetrachloride	16.5	0.14	1.18	0.12
Benzene	18.2	5.68	39.45	2.56
Toluene	16.5	3.63	30.66	2.36
Ethyl acetate	18.2	12.96	36.27	3.56
Water	20.0	0.01	0.02	0.01
Water	100.0	0.30	0.32	0.30

TABLE 34
SOLUBILITY OF *m*- DINITROBENZENE (%) IN SULPHURIC ACID OF VARIOUS CONCENTRATIONS

Temperature °C	Concentration of sulphuric acid in % H_2SO_4		
	70	80	90
0	0.60	1.4	7.15
10	0.65	1.4	7.2
25	0.75	1.7	7.9
40	0.90	1.8	9.0
50	1.00	2.2	10.1
60	1.15	2.7	11.25
70	1.40	3.5	13.40
80	1.85	4.0	16.0
90	2.05	4.8	18.6
100	3.00	6.5	22.3

TABLE 35
EUTECTICS WITH *m*- DINITROBENZENE

The second component	Weight % of *m*- DNB	m.p. °C	Author
Cyclonite	92	85.5	Urbanski and Rabek-Gawronska [4]
Nitroglycerine	17.1	5.0	Kurita and Hagui [5]
	17.5	5.0	Hackel [6]
Pentaerythritol tetranitrate	47.5	65.5	Urbanski [7]
Picric acid	66	63	Kremann and Pogantsch [8]
Tetryl	54	65.5	Jefremov and Tikhomirova [9]
sym-Trinitrobenzene	53	61.9	Hammick, Andrews and Hampson [10]
Trinitro-m-cresol	44.8	54.4	Jefremov [11]
α -Trinitrotoluene	45.5	51	Hrynakowski and Kapuscinski [12]
Trinitro-m-xylene	82.2	76.4	Jefremov and Tikhomirova [9]

Three-component systems with *m*- dinitrobenzene have been studied by Khaibashev and Bogush [12a]. They found ternary eutectics:

(1) 9% trinitro-m-xylene, 9% tetryl, 82% m-dinitrobenzene, m.p. 80.6%.
(2) 18.5% 1,8-dinitronaphthalene, 7% tetryl, 74.5 *m*- dinitrobenzene, m.p. 74.5°C.
(3) 8.5% trinitro-m-xylene, 16% pentaerythritol tetranitrate, 75% *m*- dinitrobenzene. m.p 79.5%.
(4) 16.5% 1,8-dinitronaphthalene, 12.5% pentaerythritol tetranitrate, 71% *m*- dinitrobenzene, m.p. 69°C.
(5) 5% trinitro-m-xylene, 43% picric acid, 52% *m*- dinitrobenzene, m.p. 57.6°C.

m- Dinitrobenzene can be separated from the *o*- isomer by paper-chromatography (Franc [13]), the mobile phase being composed of ethyl alcohol, water and acetic acid.

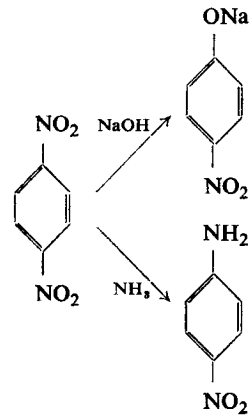
The thermochemical properties of dinitrobenzene are given on pp. 259-262 (Fig. 50).

CHEMICAL PROPERTIES

m- Dinitrobenzene is the least reactive of the three isomeric forms of dinitrobenzene, because its nitro groups are in the *meta* position to each other.

Like most nitro compounds all three isomers are resistant to concentrated acids, and fairly sensitive to alkalis.

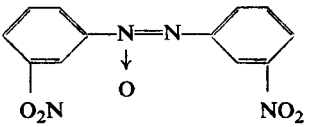
When treated with alkalis, *o*- and *p*- dinitrobenzenes are slowly converted to *o*- and *p*- nitrophenols, while with ammonia they form *o*- and *p*- nitroaniline. These reactions proceed slowly at room temperature, and more rapidly on heating.



(1)

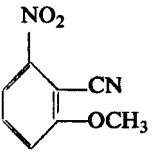
m- Dinitrobenzene does not undergo this reaction. This property was utilized in the past for separating *m*- dinitrobenzene from its isomers. Crude dinitrobenzene was shaken up with a 0.5-1.0% NaOH solution at about 80°C and the *o*- and *p*- isomers were partly extracted as corresponding nitrophenates. However, this method was not very efficient as the purified dinitrobenzene had a low melting point (80°C). It has now been replaced by sodium sulphite method.

m-Dinitrobenzene reacts with a 20% solution of sodium hydroxide only when boiled. One of its nitro groups is reduced and 3,3'-dinitroazoxybenzene is formed (Klinger and Pitschke [14]):

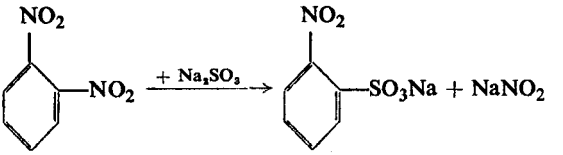


When in alcoholic solution, a molecule of *m*- dinitrobenzene adds a molecule of sodium ethoxyde to form an addition product with the formula $C_6H_4(NO_2)_2 \cdot C_2H_5ONa$ (Giua [15]).

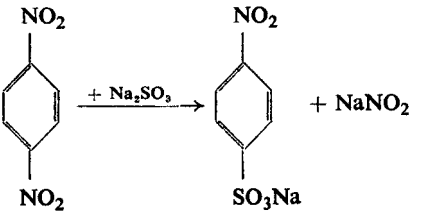
m- Dinitrobenzene reacts with potassium cyanide in methyl (or ethyl) alcohol solution, methoxynitrobenzonitrile being formed (de Bruyn [16], 1904) :



Ortho- and *p*- dinitrobenzene react with sodium sulphite toform the corre-spending nitrosulphonic acids:

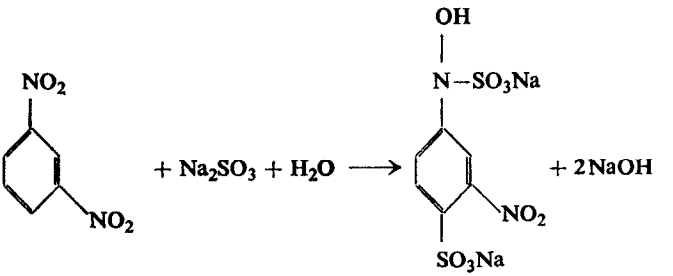


(2)

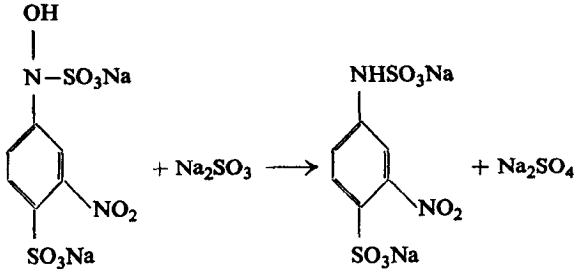


(3)

According to Golosenko (after Orlova [3]), *m*- dinitrobenzene reacts with sodium sulphite at 70°C according to the scheme:



(4a)



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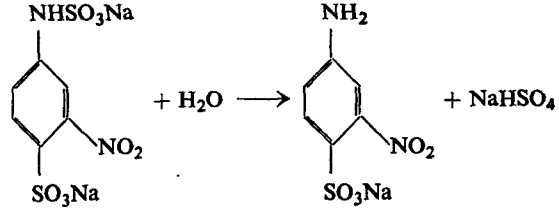
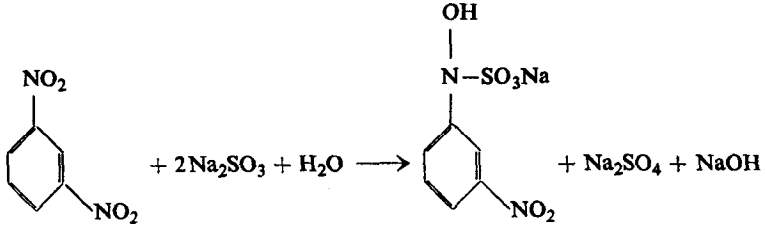
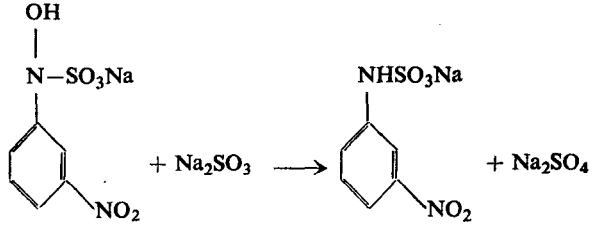


(4c)

A side reaction yields *m*- nitroaniline:



(4d)



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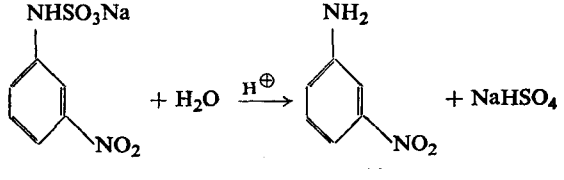
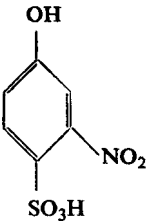


(4f)

Also as result of hydrolysis of I and II a nitrophenolsulphonic acid (V) can be formed :



V

The proportion of the compounds is: III-80%, IV-13%, V-7%.

As *m*- dinitrobenzene reacts with sodium sulphite with more difficulty, this reaction is now used for removing the *o*- and *p*- isomers from commercial dinitrobenzene (pp. 246-248).

TABLE 36

ADDITION PRODUCTS OF DINITROBENZENE ISOMERS

Second component	*o*- Dinitrobenzene		*m*- Dinitrobenzene		*p*- Dinitrobenzene	
	composition of the products	m.p. °C	composition of the products	m.p. °C	composition of the products	m.p. °C
Acenaphthene	none	—	1:1	72.3	none	
Phenanthrene	none	—	none	-	1:3	81.5
Naphthalene	none	—	1:1	50.5	1:l	ca. 117
Aniline	none	—	1:1	41.5	none	-
o- Phenylenediamine	none	—	3:2 (unstable)	58.3	none	-
m- Phenylenediamine	none	—	1:2 (unstable)	36.2	1:2	
p- Phenylenediamine			none	-	1:1	114
α -Naphthylamine	none	—	none	-	1:1	81
β -Naphthylamine	none	—	1:1	63.8	1:1	91

m- Dinitrobenzene is used for the identification of some ketosteroids (androsterone, estrone, pregnandione, cortisone etc.). A blue colour develops in the presence of potassium hydroxide. This is a modification of the Janovsky reaction suggested for this particular purpose by Zimmermann [17] (p. 207).

m- Dinitrobenzene reacts with liquid ammonia to give a purple solution containing an addition anion [68].

Dinitrobenzenes form addition products with hydrocarbons with condensed rings, as well as with aromatic amines, *p*- nitrobenzene entering the reactions the most readily, and *o*- dinitrobenzene - the least so. The addition products formed by dinitrobenzenes with various compounds have been extensively studied by Kremann and co-workers [18], Szperl and co-workers [19-20b], Giua [15]. Jefremov [9,11], Hrynakowski and KapuScinski [12].

Some of the addition products are shown in Table 36.

m- Dinitrobenzene also forms an addition product with nitrobenzene which, according to Lehmstedt [21], contains 1 mol. *m*- dinitrobenzene and 2 mol. of nitrobenzene. Its melting point is 25°C.

TOXICITY OF DINITROBENZENE

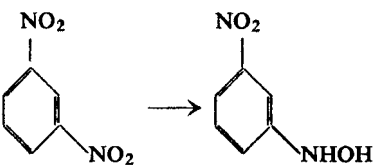
Dinitrobenzene-the commercial product consists mainly of *m*- dinitrobenzene-is one of the most toxic industrial poisons and has been the cause of a great number of fatal cases. Poisoning may be caused by inhaling the vapours or by absorption through the skin. Although dinitrobenzene has relatively little volatility, a concentration as low as 1 mg/m^3 may be sufficient to cause acute poisoning, so great care should be taken to avoid toxic concentrations.

Dinitrobenzene is a strong poison, affecting the blood and the liver. It causes the formation of methaemoglobin, which can be seen in the intense blue discolouration-cyanosis-of the lips, mucous membranes and the face of the victim.

Kiese and his colleagues [22] working with dogs, found that subcutaneous injections of *m*- dinitrobenzene given in quantities of 0.2-6 mg/kg over a long period caused anaemia, cramps, paralysis and liver damage. When experimenting on rats they were able to establish that animals suffering from chronic alcoholic poisoning, were more sensitive to *m*- dinitrobenzene than normal rats. The reverse was also true-the narcotic action of alcohol was stronger when the rats were victims of chronic *m*- dinitrobenzene poisoning.

According to Koelsch [23], chronic industrial poisoning by dinitrobenzene may appear in two forms. One of them causes degeneration of haemoglobin and in most cases recovery follows within 1-2 weeks. In exceptionally acute cases the symptoms appear rapidly and are often followed by death within a few hours.

Another form of dinitrobenzene poisoning is characterized by delayed symptoms which may appear from 1 to 3 months after exposure. Within 1-3 weeks after the first symptoms are manifested, degeneration of the liver takes place. Women are particularly liable to this form of poisoning. The illness may last for about 2 weeks in mild cases, while severe but not-fatal ones may last for 2 months. Some of the dinitrobenzene is excreted unchanged with the urine, while some of it undergoes a partial reduction in the body to a still more poisonous hydroxylamine derivative :



(5)

The medical literature (Staub [24]), dealing with industrial aspects of hygiene, reports that in the one year 1900 in a German explosives factory, 41% of the workers were poisoned by dinitrobenzene.

During World War I when dinitrobenzene was manufactured and widely

used cases of poisoning in Germany were exceptionally numerous. Poisoning cases, often fatal, would occur despite the fact that the workshops were thoroughly ventilated and the workers took such safety measures as wearing protective gloves and using helmets against inhaling the dust and vapours of the substance.

No statistical data are available for the whole period of the war. Neverthe less there are numerous fragmentary pieces of information about cases of poisoning in the manufacture and application of dinitrobenzene. For example, of about 4000 workers at one of the ammunition plants in Bavaria, nearly 2000 persons were poisoned by dinitrobenzene. In one of the workshops of another factory,

TABLE 37

STATISTICS OF CASES OF POISONING CAUSED BY DINITROBENZENE

Year	Month	Poisoned by dinitrobenzene	
		number	% of the personnel
1917	March	16	16.6
	April	15	13.6
	May	12	13.8
	June	24	30.8
	July	14	12.6
	August	19	21.2
	September	17	12.2
	October	9	8.2
	November	5	4.6
	December	3	2.3
1918	January	10	7.3
	February	19	12.5
	March	19	10.0
	April	16	11.7
	May	21	16.4
	June	19	13.3
	July	20	10.0
	August	27	17.4
	September	2	1.4
	October	6	5.8

within one month of the year 1917, 30 cases of poisoning were recorded, which corresponded to 46.8% of the personnel.

It has been observed that poisoning occurs more often on hot days than on cooler ones owing to the higher vapour pressure of the compound at higher ternperatures. For example, in one of the German factories using dinitrobenzene for alling shells, the numbers of poisoning cases recorded in several months of 1917 find 1918 are given in Table 37.

Observations by several authors have shown that women are more sensitive to dinitrobenzene than men. Poisoning by dinitrobenzene results in increased sensitivity and hence makes the sufferer more liable to repeated poisoning, especially in less resistant persons. Out of 179 workers of a German factory who were

poisoned in the year 1918, 146 of them were poisoned for the first time, 10 for the second time, 12 for the third time, and 2 women for the fourth time.

EXPLOSIVE PROPERTIES OF DINITROBENZENE

One of the characteristics of *m*- dinitrobenzene is that it shows an exceptionally low sensitivity to impact and friction. For this reason attempts have been made to use it in armour-piercing shells. However they have failed due to its two serious disadvantages; namely its great toxicity and the difficulty of effective complete detonation by initiation with an ordinary detonator. Thus, *m*- dinitrobenzene, even when compressed to a density of 1.44, requires an additional, secondary detonator.

Sensitivity to impact. According to Wöhler and Wenzelberg [25], energy of impact per unit area required to initiate 50% explosions is 19.5 kgm/cm^2 Other authors report that the relative value of the energy necessary for initiation by impact is 120 as compared with 100 for picric acid.

The explosive decomposition of dinitrobenzene may proceed, as Kast [3a] assumes, according to the equation:

$$16C_6H_4(NO_2)_2 = 10CO_2 + 38CO + 10CH_4 + C_2H_2 + HCN + 5.5H_2 + 14.5N_2 + \\ + 2NH_4HCO_3 + 33C + Q \qquad (6)$$

where Q is 870 cal/kg
V_0 is 670 l./g
t is 2500°C
f is 7035 m
Lead block expansion is 250 cm^3
The highest rate of detonation is 6100 m/sec.

PREPARATION OF DINITROBENZENE

Deville [26] first prepared dinitrobenzene in 1841 by treating benzene with concentrated nitric acid and heating it to the boiling point. Soon after that Mus-Pratt and Hofmann [27] obtained it, using a mixture of nitric and sulphuric acid for the nitration.

For a long time it was thought that a uniform substance was produced. However, m 1874 Rinne and Zincke [28], and also Körner [29] found that the *o*- and *p*- isomers are also formed along with large quantities of *m*- dinitrobenzene.

The conditions for preparing dinitrobenzene were described more fully by Beilstein and Kurbatov [29a] in 1875. They dissolved 1 part by volume of benzene in 2 parts by volume of nitric acid (sp. gr. 1.52). After cooling, 3.3 parts by volume. of sulphuric acid were added.

The possibility that a certain quantity of trinitrobenzene may be formed, as an impurity in dinitrobenzene, was reported by Hepp [30] in 1882.

Holleman and de Bruyn [31] investigated the influence of the nitration conditions on the quantity of isomers formed. When nitrating nitrobenzene with nitric acid or a nitrating mixture at temperatures below and above room temperature, they obtained the following percentages of isomers (Table 38).

Clearly, higher temperatures enhance the formation of the o-isomer at the expense of the *m*- isomer. The presence of sulphuric acid in the nitrating mixture results in a slight increase of the quantity of *m*- isomer formed and a corresponding decrease in the production of the *o*- isomer.

TABLE 38

RESULTS OF THE NITRATION OF NITROBENZENE TO DINITROBENZENE UNDER VARIOUS CONDITIONS

Nitrating agent	Temperature °C	Isomer content, %		
		meta	ortho	para
Nitric acid	0	93.2	6.4	0.5
	30	90.9	8.1	1.0
Nitric and sulphuric	0	93.9	4.8	1.7
	40	91.8	6.8	1.4

Wyler [32] has carried out a vast amount of work on the nitration of benzene. He found that in the nitration of benzene or nitrobenzene on an industrial scale, a product was obtained containing up to 12% of the *o*- and *p*- isomers. This was contrary to the generally held opinion that dinitrobenzene contains only 1% of *o*- and 3% of *p*- dinitrobenzene.

Wyler proved by a number of experiments with the nitration of nitrobenzene to dinitrobenzene, that the content of the *o*- and *p*- isomers in the product may vary from 5 to 15%, depending on the reaction conditions. At a low temperature, e.g. -17°C, equal amounts of the *o*- and *p*- isomers were formed, while higher temperatures favoured the formation of the *o*- isomer, this being on the whole in agreement with the earlier observations by Holleman and de Bruyn [31].

The results obtained by Wyler are shown in Table 39.

TABLE 39

RESULTS OF THE NITRATION OF NITROBENZENE UNDER VARIOUS CONDITIONS (WYLER)

Nitration temperature, °C	Weight of nitrobenzene g	Nitrating mixture				Period of nitration hr	m.p. °C	Composition of the product		
		Sulphuric acid		Nitric acid						
		g	Concentration %	g	Concentration %			meta	ortho	para
-17 to -10	24.6	150	105	25	96	4.00	86.9	95.1	2.5	2.4
- 5	-5	,,	,,	,,	,,	2.00	86.8	94.7	3.5	1.8
25-29	,,	,,	,,	,,	,,	1.75	85.0	92.6	5.0	2.4
65-69	,,	500	100	250	,,	1.5	83.0	89.7	7.7	3.0
65-75	,,	900	98	284	88	1.5	82.1	89.2	8.7	2.1
90-100	,,	,,	,,	,,	,,	1.50	80.0	87.0	11.8	1.2
108-113	,,	,,	,,	,,	,,	1.25	81.2	87.6	10.2	2.2
124-129	,,	,,	,,	,,	,,	0.75	79.9	85.7	13.9	0.4

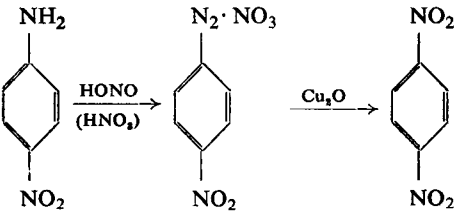
In 1933, Hetherington and Masson [33] made a systematic study of nitration of nitrobenzene to dinitrobenzene using a wide range of mixtures of sulphuric and nitric acids and water. They plotted their results on a curve of "limiting compositions" beyond which the reaction does not occur (Fig. 27, p. 154). They also showed the change in molar composition of the acid during nitration (Fig. 48). For example, an acid of initial composition will nitrate nitrobenzene until its composition moving along the parallel XY reaches Y, when it practically ceases to react. Figure 49 gives the molar compositions of the acid present in both the organic and acid layer. The rate of nitration was given in Fig. 28 (p. 155).

In practice, for the nitration of nitrobenzene, a nitrating. mixture of the composition:

HNO_3	18%
H_2SO_4	80%
H_2O	2%

is generally used, in about 10% excess over the theoretical amount.

Pure *o*- and *p*- dinitrobenzenes may be obtained from the corresponding nitroanilines in two ways: either by diazotization (Meisenheimer and Patzig [34],) or by oxidation (Bamberger and Hübner [35], Witt and Kopetschni [36]):



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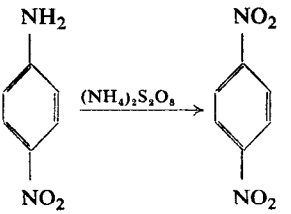


(8)

Nitration in two stages in two nitrators. In industrial practice the preparation of dinitrobenzene is commonly carried out by nitration in two stages:

Benzene -> Nitrobenzene -> Dinitrobenzene

In this way, operating conditions are safer during the process and acid control can be made more efficient.

The first operation, i.e. the nitration of benzene to nitrobenzene, has been already described (pp. 232, 233). The second stage of the process, i.e. the nitration of nitrobenzene to dinitrobenzene by the method used at Höchst (I. G. Farbenindustrie) is described below.

Nitrobenzene is pumped into a measuring tank of 5 m^3 capacity, lined with sheet lead. 3660 kg of nitrobenzene is fed from the tank to a nitrator of 10 m^3

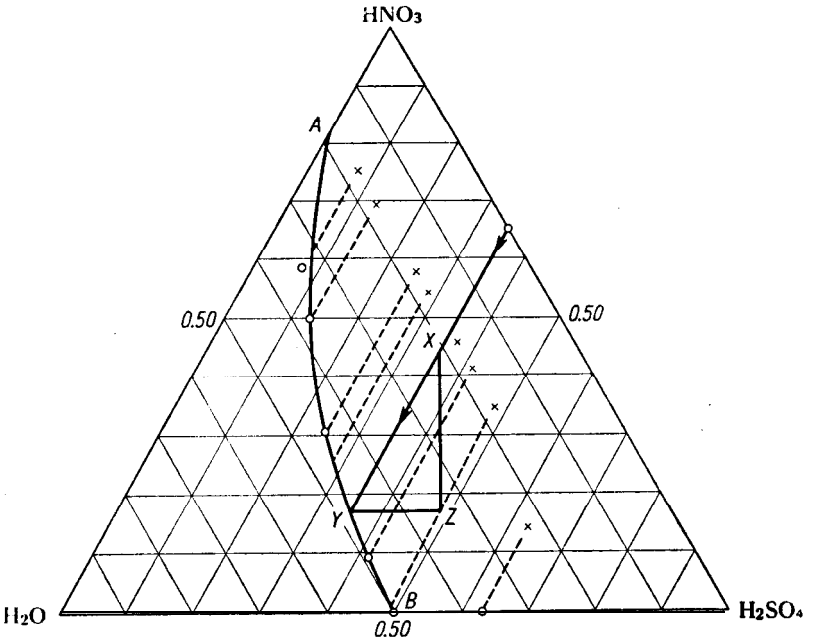


FIG. 48. Change in molecular composition of acids during nitration. AB - the curve of limiting compositions (Hetherington and Masson [33]).

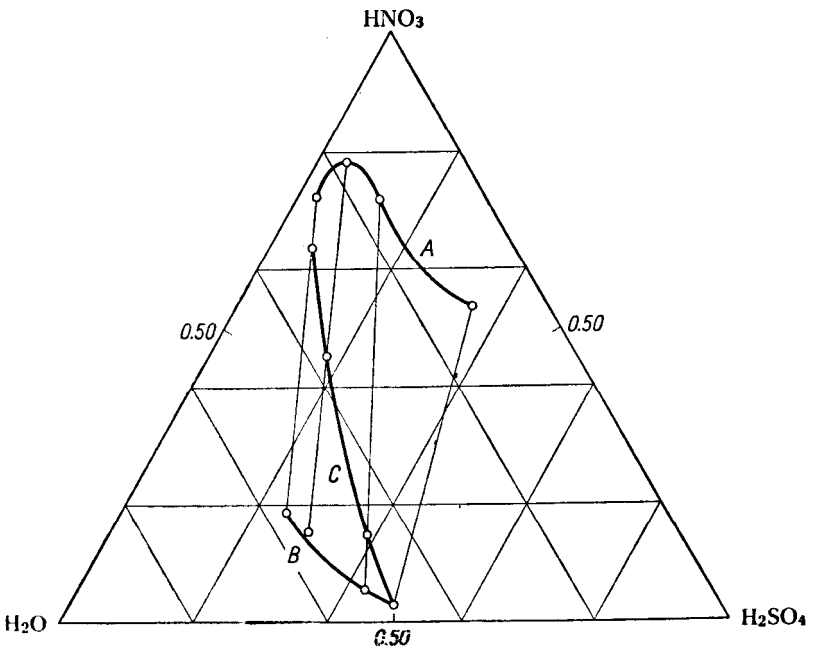


FIG. 49. Molecular compositions of acid present in the organic layer (A), acid layer (B), and in the aggregate (C). The tie-lines show the conjugate layers (Hetherington and Masson [33]).

capacity already containing the spent acid from the previous nitration. The mixture is stirred at high speed. During this operation the extraction of dinitrobenzene from the spent acid is taking place. After one hour of stirring the nitrator contents are allowed to remain at rest for 1 hr during which separation of the liquid into two layers takes place. The lower, acid layer is drained off to a spent acid tank of 25 m^3 capacity; then 6500 kg of nitrating mixture of the composition:

HNO_3	30%
H_2SO_4	67%
H_2O	3%

is fed slowly into the nitrator over a period of 4 to 5 hr. The nitrator contents are then cooled and stirred at high speed. A temperature below 40°C is maintained during the addition of acid. By the end of the operation a rise in temperature up to 80°C may be allowed. After all the acid has been added the contents of the nitrator are stirred again at 80-90°C until the nitration of nitrobenzene to dinitrobenzene has been completed. This can be achieved within 1 to 2 hr. Nitrobenzene is tested for by smelling.

After the nitration has been completed, 1000 l. of water is added gradually during 1 hr, the temperature being maintained at 80-90°C. The nitrator contents are allowed to remain at the above temperature for 1 hr. Then the lower layer, i.e. the spent acid, is drained off to a tank from which it can be transferred by compressed air to the nitrator for the next nitration operation. The product left in the nitrator is passed to a purification plant, where it is washed with alkali and purified by sulphitation. Finally the product is dried.

Purification. Washing dinitrobenzene with a solution of sodium hydroxide is carried out in the following way. The crude, molten dinitrobenzene in the nitrator is run in a tightly closed, brick lined iron vessel, heated internally by a stainless steel steam coil. From this vessel it is transferred in steam heated, stainless steel pipes to a washing tank of 16 m^3 capacity, filled with 3-4 m^3 of water and 400 1. of a 33% solution of sodium hydroxide, heated to 50°C. The dinitrobenzene is run in the washing tank over a period of half an hour and this is accompanied by continuous vigorous stirring. The temperature should not rise above 80-85°C. All the time the solution in the washing tank should be alkaline (phenolphthalein test). If all the sodium hydroxide is used up, an additional quantity of it must be added. After all the crude dinitrobenzene has been introduced to the washing tank its contents are stirred for a further period of 30 min to one hour.

Sulphitation of dinitrobenzene (Griesheim method) is carried out in the same washing tank. Cold water is run in until the temperature falls to 66°C. Then a solution of sodium sulphite, prepared by mixing 1000-1100 l. of a 40% solution of sodium hydrogen sulphite with 400-500 kg of 33% sodium hydroxide, is added.

During sulphitation a temperature of 66-73°C is maintained. After 2 hr of mixing at this temperature the contents of the vessel are cooled to 50°C. The purified dinitrobenzene crystallizes in rather large crystals. The melting point of the product should be 88-89°C. The mother liquor is pumped off through a pipe closed

by a wire gauze, which retains the dinitrobenzene crystals, while the liquor runs into an outlet pipe, through a separator where any crystals which have been carried over are retained. The dinitrobenzene in the vessel is thoroughly washed by repeated rinsing with water, which is then pumped away.

The dinitrobenzene, which is now well washed and free from the sodium sulphite and sodium nitrite formed during sulphitation, is melted and introduced to a special vessel of 15 m^3 capacity, where it is separated from residual water by decantation. It is tested to ensure that washing has been fully effective, by boiling a sample with water, followed by cooling and filtering. The filtrate should not decolorize a solution of $KMnO_4$ during a 10-min test period.

The tinal product is dried at 135°C under reduced pressure in the molten state in a drying vat of 16 m^3 capacity.

The product is cast in blocks. From the quantities of raw materials given above, 4100 kg of dinitrobenzene, melting at 88-89ºC, are obtained.

Nitration in two stages in one nitrator. The Griesheim (I. G. Farbenindustrie) process for the manufacture of dinitrobenzene differs from that of Höchst since in the latter the whole nitration starting from benzene is carried out in one cast iron nitrator of 8 m^3 capacity. The nitrator is equipped with a stirrer, rotating at 110 r.p.m., a jacket having a cooling area of 8 m^2 and a lead cooling coil of 16 m^2 area.

2200 kg of the waste acid from the previous batch are left in the nitrator and to this 1900 kg of nitrating mixture is added, the composition of which is as follows:

HNO_3	88%
H_2SO_4	11%
H_2O	1%

2200 kg of benzene are run in during a period of 4 hr while the temperature rises from 25°C to 40°C. Then the temperature is allowed to rise gradually to 60°C over a period of 1 hr. Then the stirrer is stopped, the contents are allowed to settle and the waste acid is run off to a lead lined washing vessel (A) of 12 m^3 capacity, where it is washed with benzene or nitrobenzene.

To the crude nitrobenzene left in the nitrator 5000-6000 kg of a nitrating mixture are then added gradually over 3 hr, the temperature rising from 25°C to 40°C. The mean composition of the mixture is:

HNO_3	33%
H_2SO_4	67%

The temperature should rise to 90°C and be maintained there for 1 hr. A sample is then tested by steam distillation for the presence of nitrobenzene. The amount of nitrating mixture used depends on the actual amount of HNO_3 in it and on the result of the test.

When the batch has settled the waste acid is run into a washing tank (A) where the acid from three or four nitrations has been collected and where the whole is washed with nitrobenzene.

Next the dinitrobenzene is run to a tile-lined stainless steel washing tank (B) of 12 m^3 capacity, where it is washed with 4000 l. of hot water and then with a further 4000 l. containing sufficient NaOH to give a neutral reaction. Finally it

is washed with water, and then transferred in a molten state to a purification unit. where it is dried at 120°C and 15 mm Hg. The product is crude dinitrobenzene. The amount of H_2SO_4 in the waste acid from dinitration is about 80%. After mixing with nitric acid it can be used for mononitration.

Purification. 4500 kg of molten dinitrobenzene (i.e. one charge of the nitrator) are run into a washing tank (C). The tank of 12 m^3 capacity must be made of stainless steel, lined with tiles, and fitted with a lead coated lid and a lead coated stirrer. 3000 1. water at ca. 80°C are run into it over the dinitrobenzene, with constant stirring. The whole is allowed to cool until granulation begins at ca. 70°C, the exact temperature depending on the stirrer and on the quality of the dinitrobenzene. Immediately granulation begins, 650 kg of sodium sulphite are introduced at a rate of 100 kg per 15 min. The temperature rises to 78°C and stirring must be continued for another 3 hr.

Samples should be taken, filtered, washed and dried. The setting point should not be lower than 88.5°C. If it is too low, 25-30 kg more of sodium sulphite are added.

The contents of the washing tank are cooled by circulating water within the jacket to 20-25°C. The mother liquor is pumped off through a wire gauze and the product is washed with cold water. Washing is continued until the colour changes from dark red to light yellow. The dark wash-liquors are discarded, the light ones being kept for the next batch.

The washed product is heated to 95°C and when in a molten state it is dried under reduced pressure. The drier consists of a jacketed cylindrical vessel of 12 m^3 capacity. Finally, the pure dried product is turned into flakes.

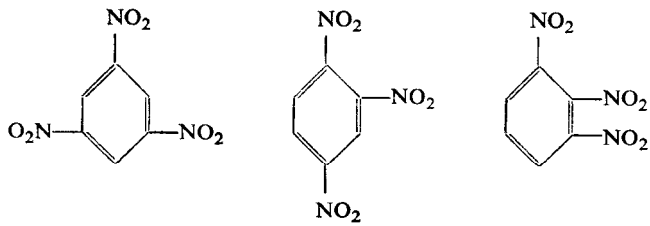
The product has the setting point 88.5-89°C.

The yield is 100 kg of crude dinitrobenzene from 48 kg of benzene (96.7% theoretical). 100 kg of pure dinitrobenzene are obtained from 118 kg of crude product. This makes an overall yield of 81.9% calculated on benzene.

The crude product, according to Griesheim's experience, contains: 85% of *meta*-, 13% of *ortho*- and 2% of *para*- isomers.

TRINITROBENZENES

Three isomers of trinitrobenzene are known: 1,3,5-trinitrobenzene (sym-trinitrobenzene), 1,2,4-trinitrobenzene and 1,2,3-trinitrobenzene:



Their melting points are: 122°C, 62°C and 127.5°C respectively.

All the isomers are crystalline, pale yellow products and are poisonous. In addition, sym-trinitrobenzene causes severe irritation of the skin. 1,3,5-Trinitrobenzene can be formed in poor yield by the action of a mixture of anhydrous nitric acid and fuming sulphuric acid on *m*- dinitrobenzene, the 1,2,4-isomer also being formed in a very small quantity. The 1,2,3-isomer can be obtained only by indirect methods.

sym-Trinitrobenzene, though the most readily obtainable as well as chemically the most stable of the three isomers, has not found practical application, although it is a powerful explosive, with an explosive power slightly higher than that of TNT. Its preparation is too expensive. In the organic chemical industry sym-trinitrobenzene is used only for the manufacture of certain intermediates. e.g. phloroglucinol.

PHYSICAL PROPERTIES OF SYM-TRINITROBENZENE

According to Jefremov and Bogoyavlenskii [37] sym-trinitrobenzene exists in two isomorphic forms, which melt at 122.5°C and 106.3°C respectively.

It forms eutectics with other high nitrated aromatic compounds and certain nitric esters (Table 40). (See also Burkhardt [65].)

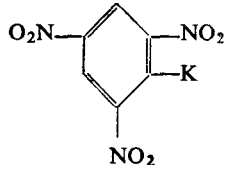
The solubility of sym-trinitrobenzene in various solvents according to Orlova [3] is given in Table 41.

The solubility of sym-trinitrobenzene in sulphuric acid of various concentrations is given in Table 42 (according to Orlova [3]).

CHEMICAL PROPERTIES OF SYM-TRINITROBENZENE

Reactions with alkalis. sym-Trinitrobenzene like other polynitro-compounds. exhibits high resistance to acids, while it reacts readily with alkalis.

It was Hepp [30] in 1882 who first found that sym-trinitrobenzene forms a dark coloured substance with sodium alcoholate. V. Meyer [38] isolated a similar substance in 1896 when treating sym-trinitrobenzene with potassium alcoholate, and assigned the following structure to it:



However, the formula could not be accepted, as, according to observations of de Bruyn [16] in 1895, the product is formed only in the presence of alcohol, and its empirical formula is $C_6H_3(NO_2)_3.CH_3OK$.

Angeli [39] suggested in 1884 that the addition of potassium alcoholate occurs through one of the nitro groups:

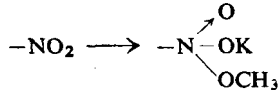


TABLE 40

EUTECTICS WITH SYM-TRINITROBENZENE

The second component	Weight % of TNB	m.p. °C	Author
m- Dinitrobenzene	47	61.9	Hammick, Andrews and Hampson[10]
Nitroglycerine	17.5	5.0	Hackel [6]
Pentaerythritol tetranitrate	70	101.1	T. Urbanski [7]

TABLE 41

SOLUBILITY OF SYM-TRINITROBENZENE (g) $C_6H_3(NO_2)_3$ IN 100 g OF SOLVENT

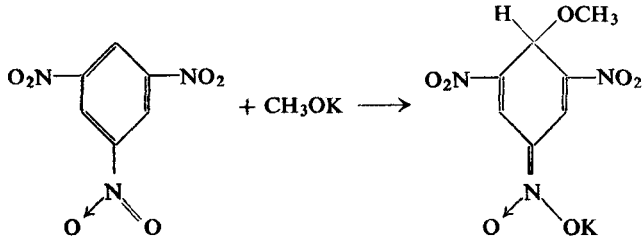
Solvent	Temperature, °C		
	17	50	100
Methanol	3.76	7.62	
Ethanol	2.09	4.57	
Ether	1.70	2.72 (at 32°)	
Acetone	59.11	160.67	
Carbon disulphide	0.24	0.44 (at 33°)	
Chloroform	6.24	18.42	
Benzene	6.18	25.70	
Toluene	11.86	46.31	
Pyridine	112.60	194.23	
Ethyl acetate	29.83	52.40	
Water	0.03	0.10	0.50

TABLE 42

SOLUBILITY OF SYM-TRINITROBENZENE IN SULPHURIC ACID

Temperature °C	Solubility (%) in sulphuric acid of concentration in % H_2SO_4			
	70	80	90	100
25	0.5	1.05	7.8	21.5
40	0.75	1.75	8.6	24.0
50	0.9	1.9	11.3	26.5
60	1.15	2.3	11.65	28.0
70	1.2	2.95	12.05	32.0
80	1.5	3.75	14.75	34.3
90	2.0	4.15	17.75	37.0
100	2.5	5.90	21.30	42.4

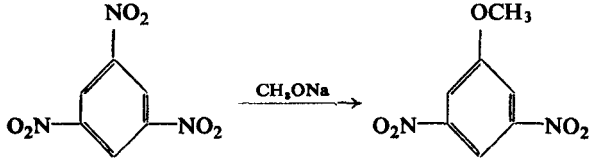
The problem was finally solved by Meisenheimer [40] in 1902, who found that by the addition of CH_3OK to trinitrobenzene an anisole derivative was formed:



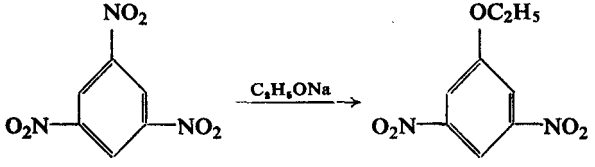
(9)

According to Meisenheimer, this formula was confirmed by the fact that the product of the addition of potassium ethoxide to trinitroanisole is identical to the product of the addition of potassium methoxide to trinitrophenetole. Meisenheimer's view was later confirmed by a number of workers, as for example Busch and Kogel [41], Bölian [42] and others (p. 203).

The reaction proceeds differently when sym-trinitrobenzene is heated with sodium ethoxide. One of the nitro groups is substituted by a methoxy or ethoxy group, 3,5-dinitroanisole or 3,5-dinitrophenetole being formed:

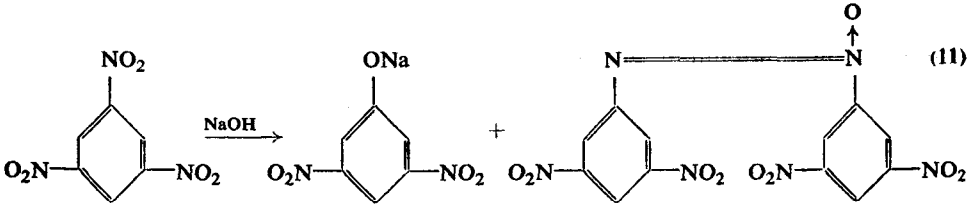


+ $NaNO_2$ (de Bruyn [16]) (10a)



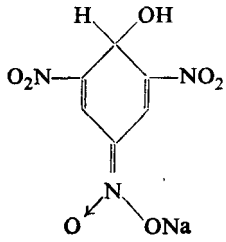
+ $NaNO_2$ (Blanksma [43]) (10b)

Similarly, when trinitrobenzene is boiled with an aqueous solution of NaOH, sodium 3,5-dinitrophenate is formed along with some tetranitroazoxybenzene (de Bruyn [16]):



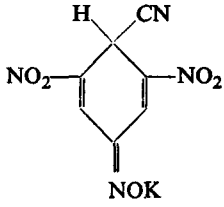
(11)

At a low temperature sym-trinitrobenzene may form an addition product with NaOH (Giua [15]). Giua ascribed to it a structure based on Meisenheimer's proposals :



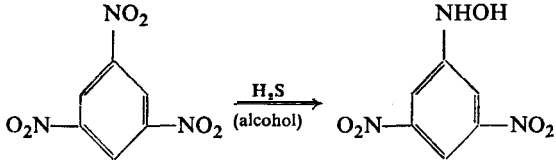
It seems possible that the products of the reaction of sym-trinitrobenzene with NaOH or alkali ethoxides are not individuals but mixtures of several compounds. For example, Busch and Kögel [41] found that sym-trinitrobenzene was able to add on not only one, but also two or three molecules of an ethoxide.

Trinitrobenzene combines with potassium cyanide to form a blood red addition product, to which Meisenheimer [40] ascribed the structure:



Oxidation. Mild oxidizing agents, such as potassium ferricyanide, convert trinitrobenzene into picric acid (p. 204).

Reduction. sym-Trinitrobenzcne, when reduced with sodium- or ammonium sulphide, forms 3,5-dinitroaniline. By treating it with hydrogen sulphide in alcoholic solution dinitrophenylhydroxylamine may be formed:



(12)

With sodium polysulphide, sym-trinitrobenzene yields tetranitroazoxybenzene along with dinitroaniline. All three nitro groups can be reduced by tin or iron in hydrochloric acid, triaminobenzenc being formed, which is the starting material for the manufacture of phloroglucinol. sym-Trinitrobenzene can react with sodium borohydride to yield trinitrocyclohexane (Severin [66]).

Reaction specific to sym-trinitrobenzene. Sym-trinitrobenzene in acetone solution rapidly produces a red colour with alkali hydroxides or ammonia. In the absence of the solvent the colour develops slowly.

Addition compounds. sym-Trinitrobenzcne readily forms well defined, often coloured compounds with hydrocarbons with condensed rings. Kremann and co-workers [18,44], Jefremov and co-workers [9,11,44a], Sudborough and Beard [44b] and their co-workers have studied most of these systems, containing sym-trinitrobenzene, by thermal analysis.

Similar compounds, for the most part coloured, are formed with aromatic artlines as well as with some phenols and aromatic alcohols.

TABLE 43
MOLECULAR COMPOUNDS WITH SYM-TRINITROBENZENE

Second component	Molecular proportion†	m.p., °C
Naphthalene	1:1	151
Anthracene	1:1	165
Acenaphthene	1:1	161
Phenanthrene	1:1	125
Fluorene	3:2	105
Aniline	1:1	125
p- Naphthylamine	1:1	161
o- Phenylenediamine	1:1	163
m- Phenylenediamine	1:1	168
p- Phenylenediamine	1:1	145.5
Diphenylamine	2:1	100.3
m- Nitroaniiine	1:1	97.5
Carbazole	1:1	203
Hydroquinone	1:1	131
Resorcinol	2:1	103
Triphenylcarbinol	3:2	134.5

† The first figure is for trinitrobenzene.

sym-Trinitrobenzene forms also an addition compound with nitrobenzene, the molecular proportion being 1:1. The product melts at 66.3°C (Hammick, Andrews and Hampson [10]).

sym-Trinitrobenzene also forms an addition product with pyridine N-oxide (Ross, Kelley and Labes [45]).

The addition products are generally unstable and can be dissociated simply by dissolution in solvents, e.g. benzene. They decompose completely into their components when treated with acids. For example, dilute acid causes quantitative separation of the amine from the nitro compound.

The cause of the colour intensity of the addition products of trinitrobenzene, as well as of other higher nitrated aromatic hydrocarbons with amines has already been discussed (pp. 221-222).

EXPLOSIVE PROPERTIES OF SYM-TRINITROBENZENE

According to Kast [3a], the explosive characteristics of sym-trinitrobenzene are exposed in the following figures:

density	1.63 g/cm^3
heat of explosion	1065 kcal/kg
volume of gases, V_0	670 l./kg
explosion temperature	3540°C
maximum rate of detonation	7000 m/sec
specific pressure, f	9665 m

The lead block test is 330 cm^3, and compared with picric acid (taken as 100), it is 108-111.

The sensitiveness to impact is slightly lower than that of TNT. According to Wohler and Wenzelberg [25], an impact energy of 12.1 kgm/cm^2 is necessary to produce 50% explosion. Thus compared with picric acid (100) its relative sensitiveness is 109, i.e. to bring about an explosion, the impact energy has to be higher by 9% than that necessary to explode picric acid.

PREPARATION OF SYM-TRINITROBENZENE

Direct nitration of *m*- dinitrobenzene. Hepp [30] who first used this method in 1887, reported that he was able to nitrate only two thirds of the dinitrobenzene used, in spite of using anhydrous nitric acid and fuming sulphuric acid.

De Bruyn [16] in 1894 could not obtain a yield higher than 50%, by reacting 500 g anhydrous nitric acid and 1000 g of fuming sulphuric acid with 60 g of *m*- dinitrobenzene, in spite of carrying out the process for 5 days (1 day at 80-100°C and the next 4 days at 110°C).

Trinitrobenzene has three good qualities as an explosive: high stability, great explosive power, and a low sensitiveness to impact and friction. There were good reasons for seeking more economic production methods. These investigations were particularly intensive during World War I.

Radcliffe and Pollitt [45a] found that on nitrating *m*- dinitrobenzene with a mixture of anhydrous nitric acid and 60% oleum at 110-120°C for 6½ hr, a 71% yield could be obtained, and that by using 20% oleum a 56% yield was obtained. According to Drumond [46], a yield amounting to only 29% theoretically can be obtained as a result of nitration with a mixture of nitric acid and 20% oleum at 130°C for 3 hr.

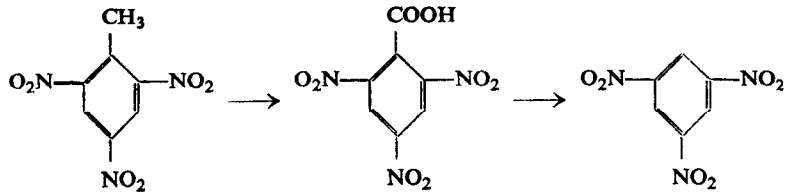
The results of Hepp, Lobry de Bruyn and Desvergnes have been confirmed by T. Urbanski and Simon [46a].

Moreover, Radcliffe and Pollitt found, that under certain conditions, the nitration of *m*- dinitrobenzene yielded a product melting at 61°C which was not the 1,2,4-isomer but, as they assumed, an "isomorphic modification of sym-trinitrobenzene".

However, this view was shown to be wrong. Gibson [47] cast a certain doubt on their statement and later T. Urbanski and Simon [46a] proved that the product melting at 61°C formed in the nitration of *m*- dinitrobenzene is simply a mixture of *m*- dinitrobenzene (35-50%) and sym-trinitrobenzene.

R. Robinson [67] reported that G. Müller nitrated *m*- dinitrobenzene to sym-trinitrobenzene by using cold anhydrous mixtures of nitric and perchloric acids.

Preparation from a- trinitrotoluene. In 1893 a patent was granted to the Chemische Fabrik Griesheim [47a] for the manufacture of sym-trinitrobenzene from trinitrotoluene. The method was based on the fact observed by Tiemann [48] and by Claus and Becker [49], that trinitrotoluene can be oxidized with nitric acid to trinitrobenzoic acid, the latter being readily decarboxylated to form sym-trinitrobenzene:



(13)

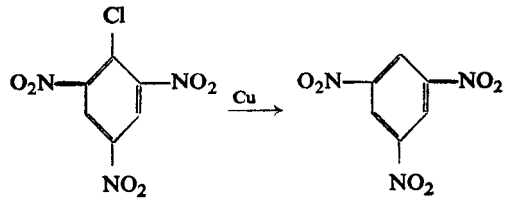
In the Griesheim method the oxidation of trinitrotoluene is accomplished by means of chromic acid in the presence of sulphuric acid, a temperature 40-50°C being maintained. By diluting the solution with water, trinitrobenzoic acid is precipitated. Boiling the acid in water results in the evolution of CO_2 and the formation of trinitrobenzene.

The Griesheim method is generally used for the laboratory preparation of sym-trinitrobenzene. However, it is too expensive to be applied in industry. Trinitrobenzene prepared in this way is much more costly than trinitrotoluene, whereas the gain in explosive power obtained is relatively small.

A less expensive method which Gamer and Abernethy [50] attribute to Koehler, consists in the oxidation of trinitrotoluene with 90-92% nitric acid in the presence of 93% sulphuric acid at 190°C. However, it requires very prolonged heating-about 40 hr. The method has not been adopted because of the considerable risk of explosion. Indeed, an explosion occurred in a factory at St. Chamas when experiments on a semi-industrial scale were carried out.

It should be mentioned that sym-trinitrobenzene is formed as a by-product of the nitration of toluene to trinitrotoluene (p. 338).

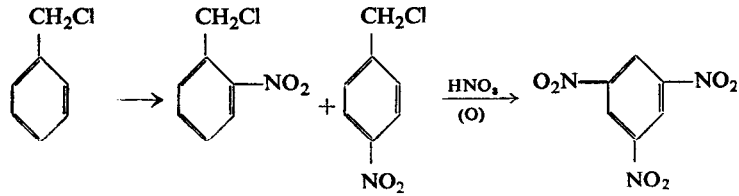
Preparation from picryl chloride. According to Ullmann and Bielecki [51] and also J. Meyer [52], trinitrobenzene may. be obtained by removing the chlorine atom from picryl chloride in the presence of copper:



(14)

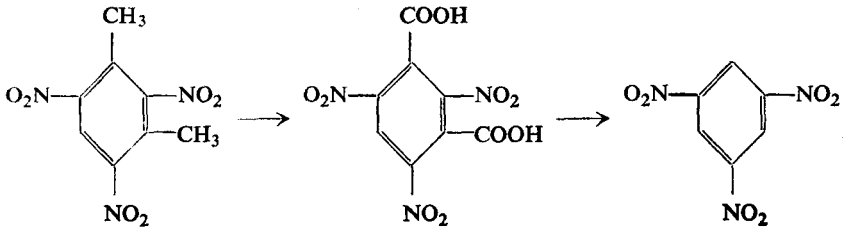
The reaction is carried out in about 85% alcohol solution at boiling point. Difficulties in obtaining picryl chloride are a drawback for applying the method industrially.

Preparation from benzyl chloride. This method has been proposed by Bronchard [53]. It consists in the nitration and oxidation of benzyl chloride:



(15)

Preparation from *m*- xylene. Giua [15] suggested sym-trinitrobenzene might be prepared by the nitration of *m*- xylene to the trinitro derivative, followed by oxidation and decarboxylation:

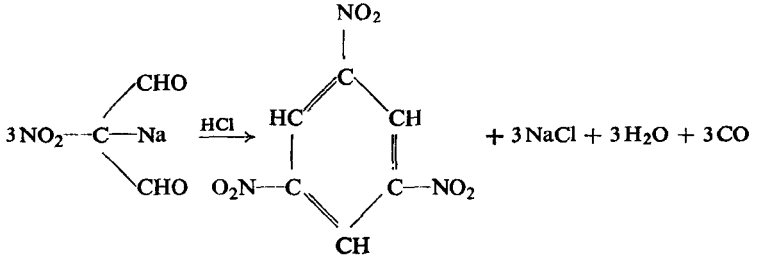


(16)

The method is rarely used, for pure *m*- xylene is not easily available in industry.

Other preparatory reactions. sym-Trinitrobenzene is also formed as a result of the prolonged treatment of benzene with nitrogen dioxide in a closed vessel (Wieland [54]).

The preparation of sym-trinitrobenzene by cyclization of nitromalonic aldehyde (Hill and Torray [55]):

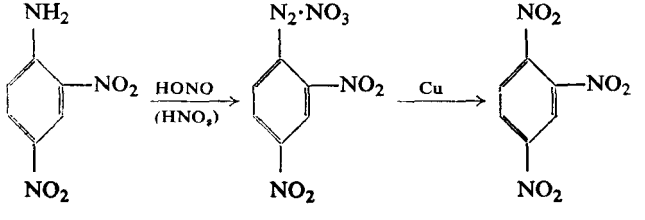


(17)

is of theoretical importance only.

PREPARATION OF UNSYMMETRICAL ISOMERS OF TRINITROBENZENE

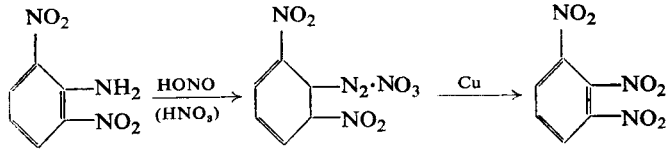
1,2,4-Trinitrobenzene may be obtained only in moderate yield by nitration of *o*- or *p*- dinitrobenzene. A product of high purity may be obtained from 2,4-dinitroaniline (Korner and Contardi [56]):



(18)

This isomer dissolves less easily in alcohol or ether than sym-trinitrobenzene. The nitro group in position 1 can readily be substituted by a hydroxyl or amino group.

1,2,3-Trinitrobenzene cannot be obtained by the nitration of *o*- dinitrobenzene. Kamer and Contardi have prepared this isomer from 2,6-dinitroaniline:

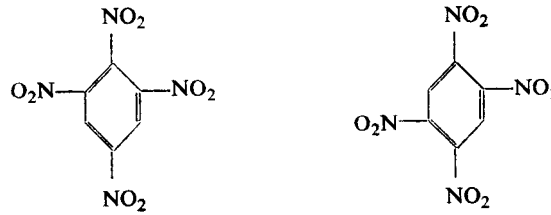


(19)

The nitro group in position 2 can readily be substituted by a hydroxyl or amine group.

TETRANITROBENZENES

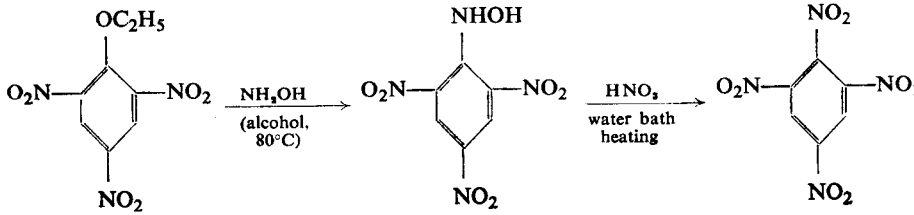
Two isomers of tetranitrobenzene are known : 1,2,4,6-tetranitrobenzene and 1,2,4,5-tetranitrobenzene:



Their melting points arc 129-130°C and 188°C respectively.

1,2,4,6-Tetranitrohenzene. It was Borsche [57] who first prepared 1,2,4,6-tetranitrobenzene in 1923, by treating picrylhydroxylamine with anhydrous nitric acid.

According to Borsche, the reaction steps are as follows:

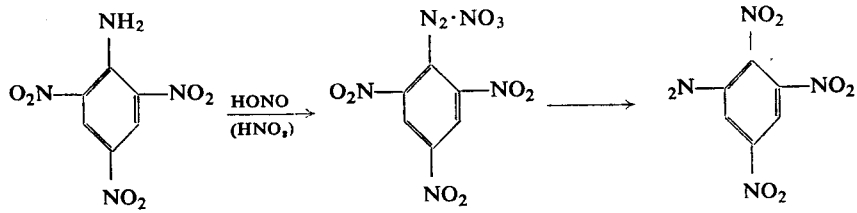


(20)

m. p. 125-126°C

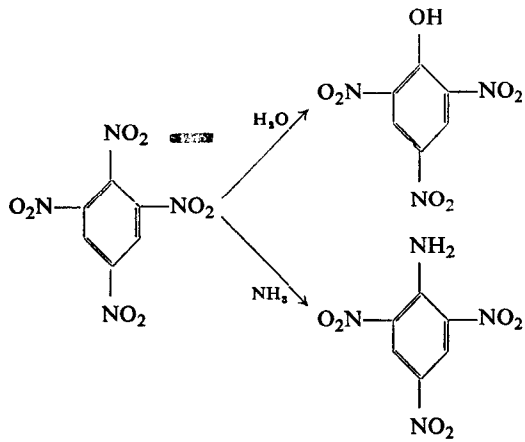
Picrylhydroxylamine is oxidized in a yield of about 60% of theory.

Holleman [58] obtained tetranitrobenzene in another way, starting from picramide:



(21)

Tetranitrobenzene is a crystalline substance, melting at 129-130°C. In the presence of moisture it is readily decomposed to form picric acid. When boiled with water it is fully converted to picric acid. It reacts with ammonia even at room temperature, forming picramide:



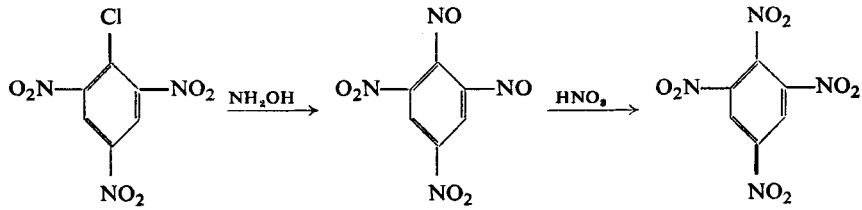
(22)

Holleman gave the following data on the explosive properties of tetranitrobenzene: sensitiveness to impact - explosion caused by a 2 kg weight falling from the height of 25 cm; expansion in the lead block = 447 cm^3.

According to other data, relative sensitiveness to impact is 67 (compared with picric acid = 100), and relative lead block test expansion amounts to 143 (picric acid = 100).

Brzozowski [59] gave additional data on the explosive properties of tetranitrobenzene. He determined the detonation rate of tetranitrobenzene, at a density of 0.7 g/cm^3 to be 5375 m/sec. At the same density, the detonation rate of trinitrobenzene is 3990 m/sec, and that of dinitrobenzene is 1795 m/sec.

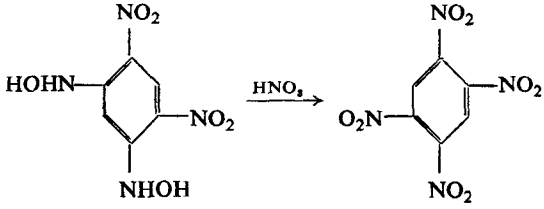
(The preparation of tetranitrobenzene was first mentioned in the literature by Nietzki and Dictschy [60] in 1900. The authors described the preparation of the new compound by the following reactions:



(23)

The product obtained melted at 116°C. However, the results have not been confirmed by the investigations of other workers. For example, Will [61] boiled 1,2-dinitroso-4,6-dinitrobenzene with nitric acid for 3 hr, but failed to observe any change in the compound. This is probably due to furoxane structure of *o*- dinitroso groups (p. 603).

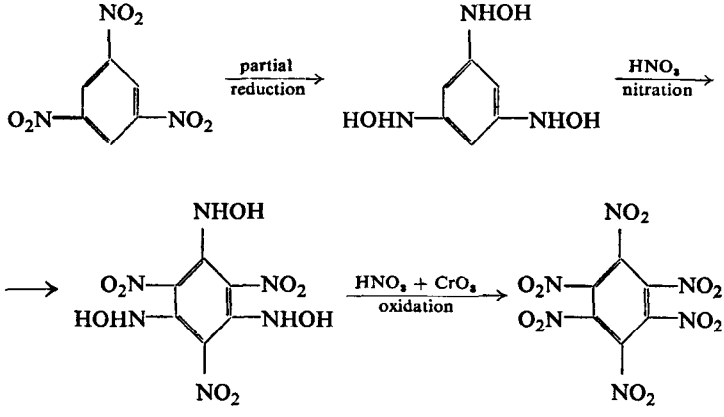
1,2,4,5-Tetranitrobenzene. This compound forms bright yellow crystals. It was prepared by Borsche and Feske [62] by the action of concentrated nitric acid on 1,3-dinitro-4,6-dihydroxylaminobenzene :



(24)

HEXANITROBENZENE

During World War II a method of synthesis of hexanitrobenzene was suggested in Germany, and the product was supposed to be manufactured on a semi-industrial scale according to the following scheme:



(25)

No details of this method are available.

Hexanitrobenzene is not stable enough for practical application, as it decomposes in the presence of moisture to form trinitrophloroglucinol.

THERMOCHEMICAL PROPERTIES OF NITRO DERIVATIVES OF BENZENE

The values of the heats of formation of benzene derivatives, given below, have been calculated from the corresponding heats of combustion (Table 44, Fig. 50).

On the basis of the above values, Garner and Abernethy [50] have calculated the corresponding heats of nitration (Table 45, Fig. 50). They have also determined the heats of crystallization, viz., for nitrobenzene they found a value of 2.78 kcal/mole, and for *m*- dinitrobenzene, 4.87 kcal/mole.

TABLE 44

HEATS OF COMBUSTION AND HEATS OF FORMATION OF BENZENE NITRO DERIVATIVES ACCORDING TO SEVERAL AUTHORS (1) -(5)

Nitro derivative of benzene	Heat of combustion (at constant volume), kcal/mole	Heat of formation (for amorphous carbon), kcal/mole
Nitrobenzene	739.9(1)	+13.1(1)
		+ 3.9(4)
		+ 6.0(5)
o- Dinitrobenzene	702.6(1)	+16.0(l)
m- Dinitrobenzene	699.4(1)	+19.2(t)
		+24.2(2)
		+ 8.6(4)
p- Dinitrobenzene	692.5(1)	+26.1(1)
sym-Trinitrobenzene	655.6(1)	+21.1(1)
	666.1(1)	+25.8(2)
		+23.0(3)
1,2,4-Trinitrobenzene	675.9(1)	+10.8(1)

(1) Gamer and Abemethy [50].
(2) Kast [3a].
(3) Berthlot and Matignon [63].
(4) Swarts [64].
(5) Chem. Techn. Reichsanstalt [65].

TABLE 45

HEATS OF NITRATION OF BENZENE AND ITS NITRO DERIVATIVES

Starting product	Nitration product	Heat of reaction kcal/mole
Benzene	Nitrobenzene	+27.0
Nitrobenzene	*m*- Dinitrobenzene	+25.6
Nitrobenzene	*o*- Dinitrobenzene	+22.4
Nitrobenzene	*p*- Dinitrobenzene	+32.5
m- Dinitrobenzene	sym-Trinitrobenzene	+21.4
o- Dinitrobenzene	1,2,4-Trinitrobenzene	+14.3
p- Dinitrobenzene	1,2,4-Trinitrobenzene	+ 4.2

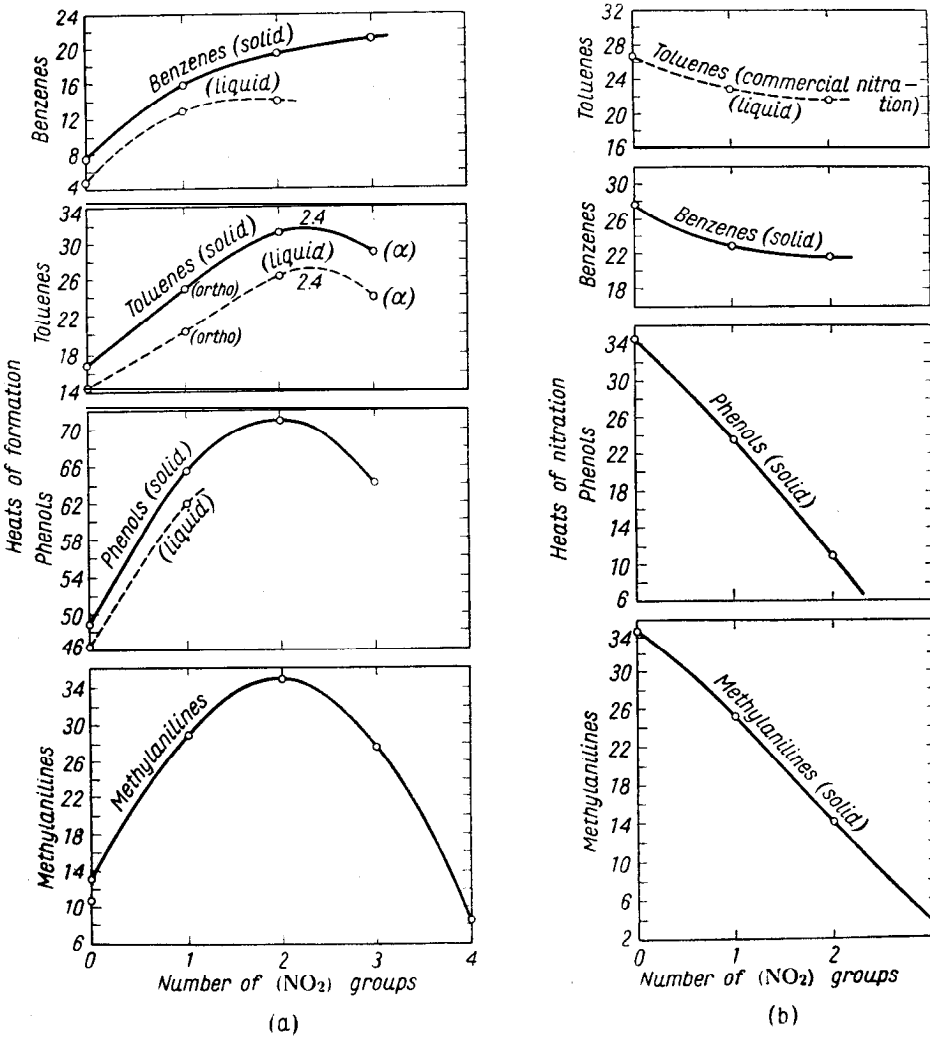
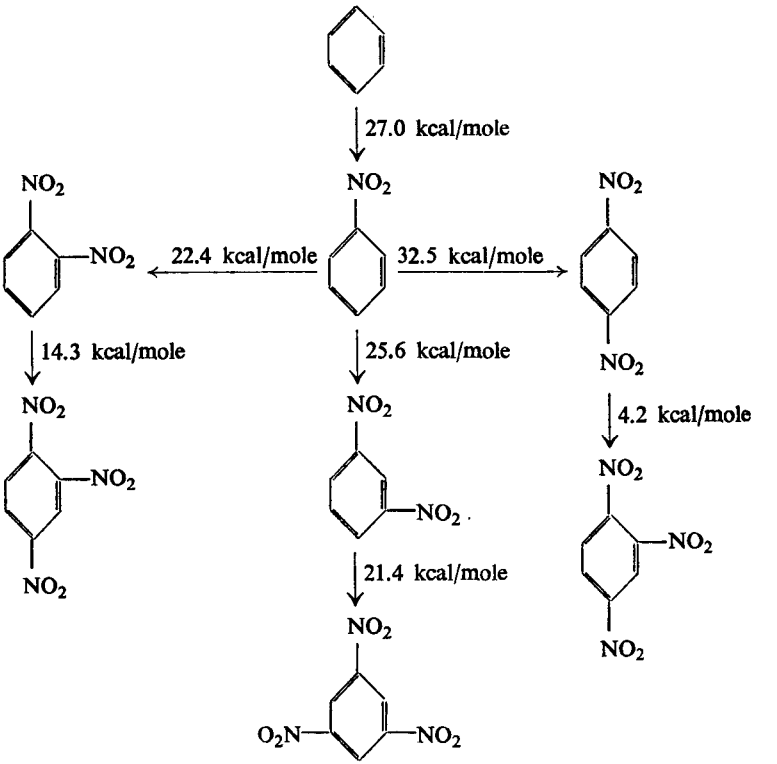


FIG 50. Heats of formation of nitro derivatives of benzene and toluene (a) and heats of nitration of benzene and toluene (b) in kcal/mole. (Garner and Abernethy [50]).

On the basis of these data the following diagram of the thermochemistry of the nitration of benzene to trinitrobenzene may be presented:



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BIOS 1144, I. G. Farbenindustrie (Griesheim and Leverkusen).

CHAPTER VIII

NITRO DERIVATIVES OF TOLUENE

ONE, two, or three nitro groups can be introduced by direct nitration of toluene. Tetranitrotoluene can be obtained only by indirect methods.

Of all nitro derivatives of toluene, trinitrotoluene is the most important as an explosive. It is by far the most often used high explosive among those derived from aromatic compounds. It is popular because it is simple and relatively safe to manufacture, and has high explosive power, and above all because its high chemical stability and low sensitiveness to impact and friction make it safe to handle. In addition, its toxicity is low and thus it compares favourably in this respect with the nitro derivatives of benzene.

NITRATION OF TOLUENE

Nitration of toluene has this specific feature: the presence of a methyl group greatly facilitates the nitration as compared with benzene. The reaction of introducing the first nitro group therefore proceeds very quickly. In addition to this. the methyl group is readily oxidized. Mononitration results in the oxidation of the ring and the formation of cresols (as in the case of benzene, which is oxidized to phenol). The oxidation reactions proceed especially readily under drastic conditions which introduce several nitro groups at a high temperature.

Sometimes, for example, if the nitration mixture is poor in nitric acid, tar formation may take place readily. It may also occur if an insufficient amount of the nitration mixture (calculated on HNO_3) has been used for the nitration. For this reason it is preferable to use mixtures richer in HNO_3, and to use a distinct excess of the nitrating mixture. On the other hand, both these factors (high content of HNO_3, and excess of nitrating mixture) favour oxidation processes in practice; therefore, limits are applied, i.e. nitrating mixtures should not be too rich in HNO_3, and a very slight excess (e.g. 1-2%) of it should be used.

Kostevich and Sapozhnikov [1] have carried out extensive studies on the nitration of toluene to mononitrotoluene, using nitrating mixtures of various compositions and determining the composition of mixtures leading to dinitrotoluene. All the reactions were carried out under similar conditions. The results are given in a

diagram which shows the influence of the composition of the nitrating mixtures on the product obtained (Fig. 51).

As Gorst [2] points out, it is advisable to relate the nitration results to the composition of the nitrating mixture at the moment when the organic substance has ceased being nitrated. Gorst presented the corresponding results in a diagram (Fig. 52).

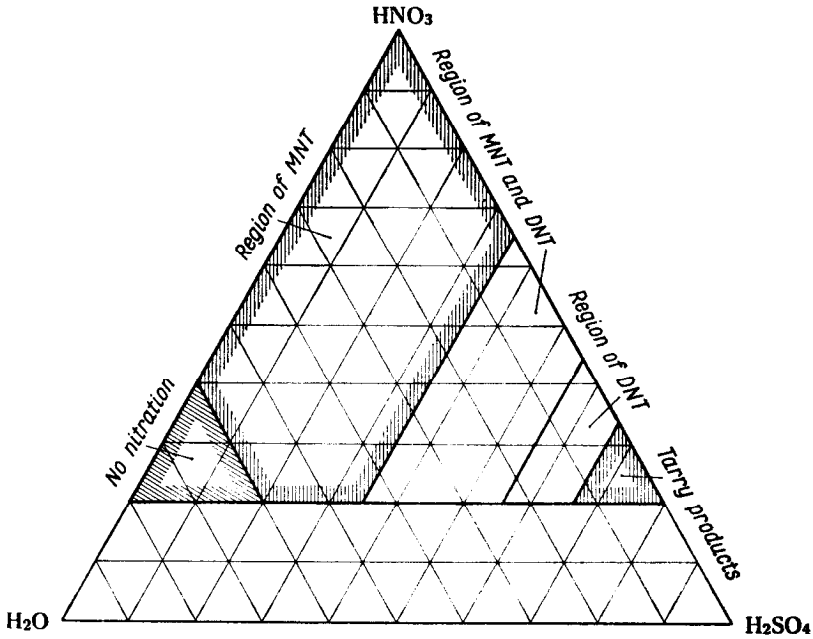


FIG. 51. Nitration of toluene with HNO_3-H_2SO_4-H_2O mixtures (Kostevich and Sapozhnikov [1]).

There is an important feature of nitrating toluene to nitrotoluenes, namely the very low solubility of toluene and nitrotoluenes in nitrating mixtures. Therefore the nitration proceeds in a two phase system and the rate of nitration depends greatly on dispersion which in turn depends on keeping the two phases efficiently stirred. Attention has previously been drawn to the importance of stirring on the yield of nitrotoluene (Fig. 25, p. 153).

Orlova [2a] gives a similar but fuller figure depicting the change of yield of nitrotoluene against the rate of stirring (Fig. 53). This relationship was established when toluene was nitrated for 30 min with an acid mixture: 11% HNO_3, 64% H_2SO_4, 25% H_2O (Φ = 69%) with a nitrating acid/toluene ratio of 3, at 30°C.

The ratio r = nitrating acid/toluene is also of importance and should be as high as economic considerations permit. The ratio r is given in Fig. 54. Here toluene was nitrated for 50 min with an acid mixture: 27% HNO_3, 55% H_2SO_3, 18% H_2O (Φ = 68%) at 30°C.

The distribution coefficient of HNO_3 between the toluene and acid layers is 0.066 at 5°C and the concentration of sulphuric acid 70% H_2SO_3. At lower acid concentrations it is practically zero. This means that on heterogeneous nitration nitric acid passes into the organic layer only in small quantities. Therefore there is practically no nitration in this layer.

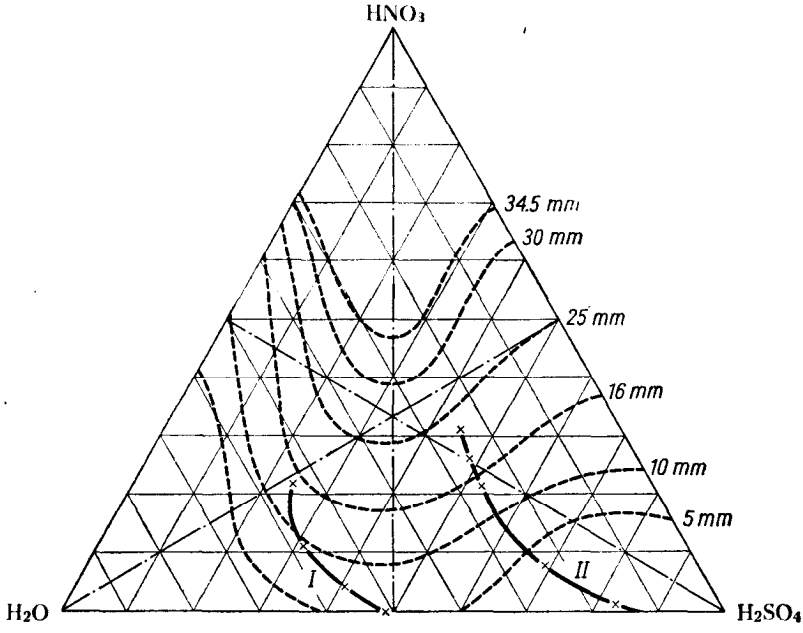


FIG. 52. Nitration of toluene with HNO_3-H_2SO_4-H_2O mixture, at temperature, of di- and trinitration 65° and 80°C respectively. Area between I and II - dinitration, to the right of II - trinitration (Gorst [2]).

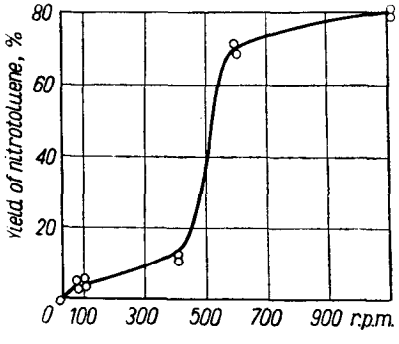


FIG. 53. Influence of the rate of stirring on the rate of nitration of toluene (Orlova [2a]).

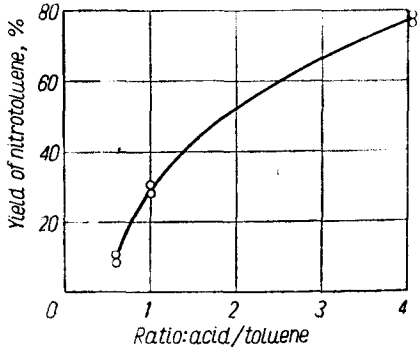


FIG. 54. Change of yield of MNT with the ratio acid/toluene (Orlova [2a]).

The reaction most probably occurs on the surface dividing the two reacting layers. The rate of nitration is therefore determined by the concentration of reactants on the surface. This in turn is determined by the rate of diffusion of two phases.

The rate of nitration is plotted against temperature of nitration in Fig. 55 (nitration mixture with Φ = 70.9%, r = 7.9, time 30 min) and the rate of nitration against the factor Φ, - in Fig. 56. Here two curves are given: one for a homogeneous

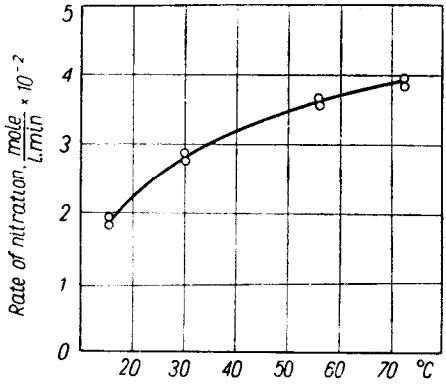


FIG. 55. change of the rate of nitration of toluene with temperature (Orlova [2a]).

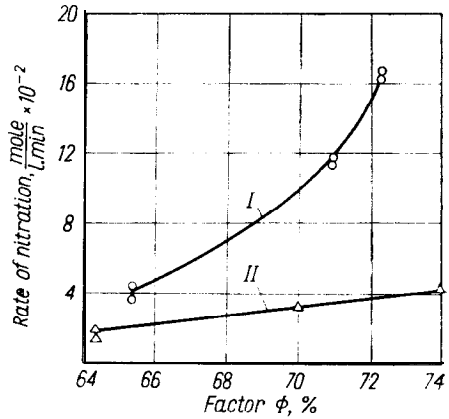
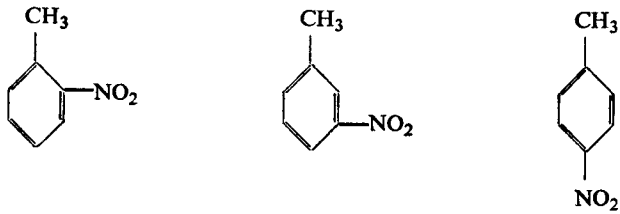


FIG. 56. Influence of the factor @ (nitrating activity) on the rate of nitration of toluene: I - in a homogeneous system, II - in a heterogeneous system (Orlova [2a]).

system (nitrating mixture of low H_2SO_4 and HNO_3 content) and another one for a heterogeneous system (the usual nitrating mixture with a high H_2SO_4 content). The change in the rate of nitration with Φ is particularly significant in the homogeneous system.

MONONITROTOLUENES

Three isomers of mononitrotoluene, *ortho-*, *meta-*, *and para-*, are known.



PHYSICAL PROPERTIES

The ortho-isomer can exist in the α -form, melting at -10.5°C, and in the β -form, melting at -4.l°C. The melting point of the meta-isomer is 16°C, and that of the *para-* isomer 52°C. The boiling points of the *ortho-*, *meta-*, and *para-* isomers are 222, 230 and 238°C respectively.

All three isomers are pale yellow substances, with the smell characteristic of mononitro compounds. They are soluble in most organic solvents. The solubility of technical MNT in sulphuric acid is shown in Table 46. Due to the presence of a methyl group, the isomers are much less toxic than nitrobenzene (p. 260).

TABLE 46

SOLUBILITY OF TECHNICAL MNT (MIXTURE OF ISOMERS) IN SULPHURIC ACID (GORST [2])

Concentration of sulphuric acid % H_2SO_4	Solubility	
	at 20°C	at 50°C
50	0.04	0.08
75	0.50	0.81
80	1.56	2.09
83	2.73	12.28
88	19.50	20.14
90	33.20	33.90

THERMOCHEMICAL PROPERTIES

Garner and Abernethy [3] give the following thermochemical data for the isomers of mononitrotoluene :

TABLE 47

HEATS OF COMBUSTION AND HEATS OFFORMATION OF MONONITROTOLUENE ISOMERS

Isomer	Heat of combustion (at constant volume) kcal/mole	Heat of formation kcal/mole
o- Nitrotoluene (liquid)	897.0	+ 2.0
m- Nitrotoluene	892.9	+ 6.1
p- Nitrotoluene	888.6	+10.4

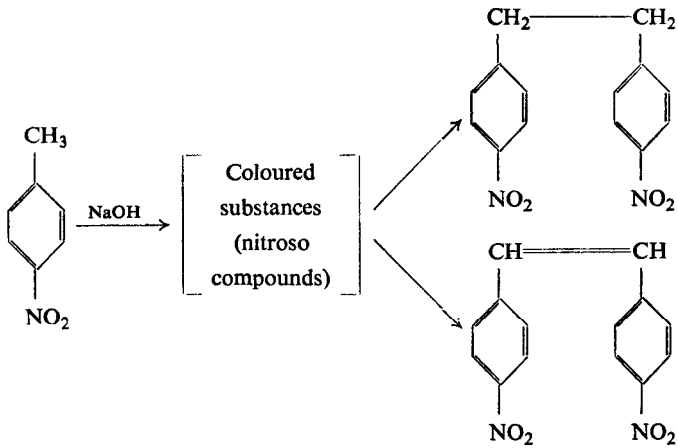
From these data Gamer and Abemethy have calculated the heats of nitration of toluene (Fig. 50 p. 261):

ortho nitration	+25.3 kcal/mole
meta nitration	+29.4 kcal/mole
para nitration	+33.7 kcal/mole

CHEMICAL PROPERTIES

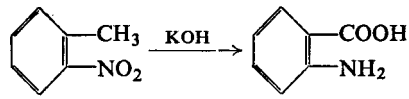
Nitrotoluene is unaffected by acids but oxidized by strong alkalis (e.g. NaOH), dibenzyl and stilbene derivatives being formed (Bender and Schultz [4], Fischer and Hepp [5]). Intensely coloured substances appear transiently, to which the

nitroso structure is ascribed (Fischer and Hepp [5], Green and Crossland [6]). They are easily oxidized by atmospheric oxygen to give nitro derivatives of dibenzyl and stilbene:



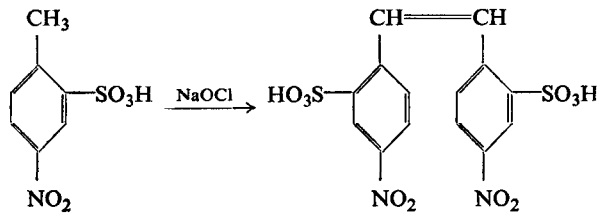
(1)

On melting with anhydrous KOH the oxidation of the methyl group takes place. with simultaneous reduction of the nitro group:



(2)

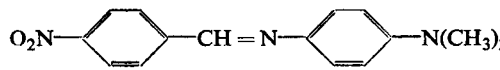
By treating a sulpho derivative of *p*- nitrotoluene with NaOCl the corresponding nitrostilbenesulphonic acid is obtained:



(3)

This is a valuable intermediate in the manufacture of direct dyes.

The methyl group in nitrotoluene is activated by the nitro group and can react, for example, with *p*- nitrosodimethylaniline to form an anil:



TOXICITY

Nitrotoluenes are considered to be toxic substances, though their toxicity is considerably lower than that of nitrobenzene. It has been suggested that this should be ascribed to the ease with which nitrotoluene is oxidized in the human body to nitrobenzoic acid, which is only slightly toxic.

PREPARATION OF MONONITROTOLUENES

In the nitration of toluene all three isomers are formed, the *o*- isomer being the predominant product. The proportion of isomers formed depends to some extent on the nitration temperature.

It was Pictet [7] who first observed, in 1893, that when nitrating toluene with a mixture of nitric and sulphuric acids at -5°C, relatively more *p*- isomer could be obtained than at 0°C.

Hollernan and Arend [8] observed the following relationship between the composition of the product of mononitration of toluene and the temperature (Table 48).

TABLE 48

RELATIONSHIP BETWEEN THE COMPOSITION OF THE MONONITRATION PRODUCT OF TOLUENE AND THE TEMPERATURE

Temperature °C	Composition of the product		
	o- isomer content, %	*p*- isomer	*m*- isomer
-30	55.6	41.7	2.7
0	56.0	40.9	3.1
+30	56.9	39.9	3.2
+60	57.5	38.5	4.0

W. W. Jones and Russel [9] determined experimentally the rate of nitration of toluene at 0°C and 30°C. Then they calculated the relative values of the A coefficient in the well known Arrhenius formula applying the conclusions of Bradfield and B. Jones (p. 65) derived from the formula:

$$A_o = 2.90\ A_m$$
$$A_o = 2.70\ A_m$$

From this they calculated the compositions of the products obtained by mononitration of toluene at -30°C and +60°C, as well as the differences in the activation energies :

$$E_m - E_o = 917 \text{ cal/mole/degree}$$
$$E_m - E_p = 1103 \text{ cal/mole/degree}$$

From these data the following rule can be derived: a lower nitration temperature causes an increase of the *p*- nitrotoluene content in the product at the cost of the *o*- and *m*- isomers.

Orlova [2a] gave similar figures:

at 30°C the proportion of *m*- nitrotoluene was 4.6%
at 55°C , ' , ' , 5.3%
at 70°C , ' , ' , 7.5%

The composition of the nitrating mixture also has an influence on the composition of mononitrotoluene. The proportion of *m*- nitrotoluene is reduced by an

increase of the factor Φ. Figure 57 gives the proportion of *m*- nitrotoluene when acids with 10% HNO_3 and various concentrations of H_2SO_4 were used at 55°C for a period of 100 min. The factor varied from 46% to 82.7%.

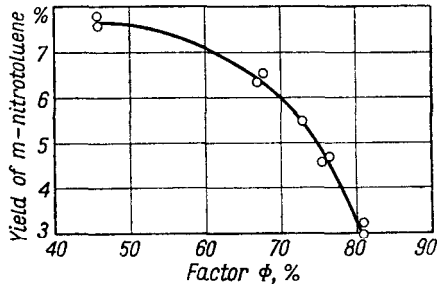
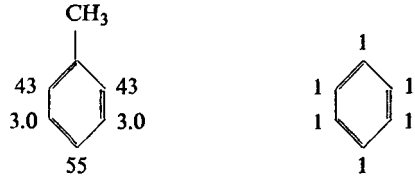


FIG. 57. Influence of the factor Φ (nitrating activity) on the yield of *m*- nitrotoluene (Orlova [2a]).

According to Ingold [9a], the relative rate of nitration on each nuclear position of toluene can be illustrated by the diagram where the rate of attack on one nuclear position of benzene has been made the unit:



R. M. Roberts, Browder, and Kobe [10] carried out a number of experiments using isotope dilution analysis to determine the proportion of *m*- nitrotoluene formed in the course of nitration of toluene.

They nitrated radioactive toluene-l-^{14}C with a mixture of nitric and sulphuric acid at 0°, 30°, 45° and 60°C. After nitration the whole was diluted, with water and steam distilled. Thus mononitro-products were separated from unnitrated toluene and dinitro products. The weighted sample of isomeric mononitrotoluene was diluted with a known quantity of non-radioactive *m*- nitrotoluene and the mixture was distilled through an efficient micro-fractionating column in order to recover a pure sample of *m*- nitrotoluene. The *m*- nitrotoluene was oxidized by dichromate-sulphuric acid mixture to *m*- nitrobenzoic acid and this material was radio-assayed. The proportion of *m*- nitrotoluene in the mixed nitrotoluenes was calculated from the formula

$$\%\ m\text{- nitrotoluene} = \frac{100x}{y(a/b-1)}$$

where

x is the weight of *m*- nitrotoluene diluent,
y is the weight of mixed nitrotoluenes diluted,
a is the molar radioactivity of the toluene-1-^{14}C nitrated,
b is the molar radioactivity of the *m*- nitrobenzoic acid.

The results from nitration at four different temperatures are given in Table 49.

TABLE 49

Temperature °C	Yield of mixed nitrotoluenes	% of *m*- nitrotoluene in mixed nitrotoluene
0	100	2.08
30	92	3.44
45	84	4.18
60		4.70

Noelting and Forel [11] found that the content of *p*- nitrotoluene increased gradually with increase in the HNO_3 content of the nitrating acid. Thus, when nitrating toluene with a mixture of nitric and sulphuric acids, the authors obtained 60% of the *p*- isomer but if nitric acid alone was used, 66% of *p*- nitrotoluene was obtained.

The effect of temperature and of the composition of the nitrating mixture on the quantity of *m*- nitrotoluene formed has been the subject of numerous studies. The results are shown in Table 50.

The order of introducing the reagents may also affect the composition of the nitration product. For example, if the toluene is added to the acid, then the first portions of toluene come into contact with a large excess of acid, and the nitration process may proceed beyond mononitration resulting in a mixture of di- and mono-nitrotoluene. If the amount of HNO_3 used has been calculated accurately, the last portions of toluene may be left unnitrated and the resultant product may not be uniform. If, on the contrary, the acid is added to the toluene, an excess of acid cannot occur, since each portion added reacts with the toluene very quickly.

TABLE 50

INFLUENCE OF TEMPERATURE AND COMPOSITION OF NITRATING MIXTURES ON *m*- NITROTOLUENE FORMATION

Nitration temperature °C	*m*- Nitrotoluene content, %					
	(1)	(2a)	(2b)	(2 c)	(3)	(4)
-30	3.5	-	-	-	-	2.97
0	3.9	2.5	4.5	3.3	3.7	5.68
20	-	4.3	4.5	3.9	-	-
30	4.4	-	-	-	4.4	4.39
40	-	-	4.2	--	-	-
50			4.3			-
60	5.1	-	-	-	-	4.90

(1) Hollemart, Vermeulen, de Mooy [12].

(2) Gibson. Duckham, Fairbairn [13]: (a) -nitration with 94% nitric acid; (b) - nitration with a mixture: HNO_3-23.8%. H_2SO_4-58.7%. H_2O-17.5%; (c)-nitration with a mixture: HNO_3-13.7%. H_2SO_4-64.4%. H_2O--21.9%.

(3) Ingold. Lapwotth, Rothstein and Ward [14] -nitration in acetic anhydride and nitromethane.

(4) W. W. Jones and Ruse1 [9] -nitration with a mixture: HNO_3-5.35%, HNO_2-1.75%. H_2SO_4-71.4%. H_2O-21.5%.

For TNT manufacture the presence of *m*- nitrotoluene in mononitrotoluene is naturally undesirable, as it is a source of unsymmetrical trinitrotoluenes.

Therefore, it would be preferable to apply a nitration method in which the *m*- isomer would not be formed at all, or only in an insignificant quantity. But as Table 50 indicates, this is impossible to achieve by nitrating with a mixture of nitric and sulphuric acids.

The fact that in the nitration of toluene with a solution of nitric acid in acetic anhydride, a mixture of 88% of *o*- and 12% of *p*- nitrotoluene, i.e. a mixture free from *m*- nitrotoluene, can been obtained, has been mentioned in the literature only once (Pictet and Khotinsky [15]).

T. Urbanski and his co-workers [16] recently confirmed this observation and reported the following nitration conditions:

composition of the nitrating mixture	68% of acetic anhydride 32% of nitric acid
excess of nitrating mixture (calculated on HNO_3)	10%
temperature of nitration	10°C
nitration period	2 h r

The mixture of *o*- and *p*- nitrotoluene they obtained was free from the *m*- isomer. The authors used it for further nitration, and found that the resulting trinitrotoluene was of much higher purity than that produced from mononitrotoluene according to the conventional industrial method.

An interesting method of reducing the proportion of *m*- nitrotoluene was developed by Orlova [2a]. It consists in adding sodium nitrite to the nitrating mixture. The results of these experiments are given in Table 51.

The nitration was carried out using acid with 10% HNO_3, for 100 min at 55°C.

TABLE 51

% $NaNO_2$	0	1.5	3.0	4.5	5.9	8.6	11.0
Proportion of *m*- nitrotoluene	5.4	4.3	4.1	3.5	2.8	2.1	2.6
Setting point of TNT, °C	78.0	78.6	78.75	78.75	78.93	78.2	77.9

Recently Kobe and Lakemeyer [17] drew attention to the fact that nitrating mixtures used for mononitration of toluene prepared spent acid from trinitration contain 14-17 wt. % of nitrosylsulphuric acid. They investigated the influence of nitrosylsulphuric acid, $SO_2(OH)ONO$, on the rate of mononitration of toluene. The rate at 35°C is at a maximum at ca. 4.0 mole % of nitrosylsulphuric acid.

More dilute nitric acid, when used for nitration, favours side reactions, primarily oxidation reactions, yielding benzoic acid. According to Konovalov [18], if a 70% nitric acid (sp. gr. 1.42) is used for the nitration of toluene, nothing but benzoic acid is formed.

According to the same author, nitrating with a more dilute nitric acid (e.g. 32%, sp. gr. 1.32) at 105°C leads to the formation of phenylnitromethane, i.e. nitration takes place in the side chain.

When nitrating toluene with nitrogen dioxide in the liquid or gaseous phase, nitrotoluene along with phenylnitromethane is obtained. As Topchiyev [19] reported. the following yields expressed as per cent theoretical, were obtained, using a large excess of N_2O_4 (200 g for 40 g of toluene) (Table 52):

TABLE 52

At temperature °C	Phenylnitromethane %	Nitrotoluene %	Unreacted toluene %
14-15	9	46.2	**40**
105-110	5	17	3

INDUSTRIAL METHODS OF NITRATION OF TOLUENE

Various methods of preparing nitrotoluenes for subsequent nitration to TNT are described below (pp. 348, 357) where methods of manufacturing TNT are discussed.

Here only those methods are reviewed which are used industrially for preparing the pure isomers : *o*-, ***m*-,** and *p*- nitrotoluene.

In industrial practice nitrating mixtures of the composition: 28-62% HNO_3, 56-21% H_2SO_4, 5-20% H_2O are used for the nitration of toluene.

Usually more of the mixture is used for nitration than theory demands, e.g. a 1-5% excess is applied so that the ratio of HNO_3 used to HNO_3 calculated varies from 1.01 to 1.05. An excess of the nitrating mixture not only favours complete nitration, but also inhibits the formation of undefined, dark coloured tarry by-products, which are readily formed if an insufficient amount of nitrating acid is used. Toluene may be added to the acid or vice versa.

The latter operation (adding acid to toluene) favours the formation of tarry products (see p. 266) but at the same time the formation of higher nitrated products is avoided, as the toluene is never in contact with an excess of acid.

A temperature within the range 25° to 40°C is maintained during mixing. Then it is raised to 60°C and maintained thus for 30 min to 1 hr. After cooling the reaction mass to 25-30°C, nitrotoluene is separated from the waste acid in a separator, the nitrotoluene being the upper layer.

A commonly used method of obtaining TNT is the direct nitrating of a mixture of the three isomers of nitrotoluene. Details are given later (Chapter IX) in the description of the manufacture of DNT and TNT. The purification of TNT from unsymmetrical derivatives of *m*- nitrotoluene consists as a rule in the sulphitation of di- or, more often, tri-nitrotoluenes or in crystallization of the trinitro-products.

However, in factories producing dye intermediates, the isomers of nitrotoluene

are separated individually, as all three are raw materials for the manufacture of the corresponding toluidines and tolidines, which are valuable dyestuffs intermediates.

Recently, as the disposal of large volumes of toxic waste waters from the purification of TNT by sulphitation has. become a problem (p. 390), new ways are being sought for the manufacture of TNT free from the unsymmetrical isomers. Apart from the possibility, mentioned above, of the utilization of nitrotoluene obtained by nitrating toluene with a mixture of acetic anhydride and nitric acid, factories TNT are now tending to separate nitrotoluene isomers by methods similar to those applied in the manufacture of dyestuffs intermediates.

This separation may be accomplished in two ways:

(1) By fractional distillation (under reduced pressure, if possible).

(2) By freezing. When the mixture has been cooled to about -12°C, *p*- nitrotoluene crystallizes out, while the *o*- and *m*- isomers remain liquid. Further cooling results in the crystallization of *o*- nitrotoluene, while the *m*- isomer remains liquid, forming an eutectic with the *o*- isomer.

The Griesheim (I. G. Farbenindustrie) method, described below, may be cited as an example of an industrial method of preparing and separating nitrotoluenes.

3000 1. of toluene are run into a nitrator of 12 m^3 capacity. Mixed acid of composition :

HNO_3	28-32%
H_2SO_4	52-56%
H_2O	20-12%

is added in over a period of 8 hr at a temperature of 25°C. The amount of acid is 99% of the theoretical, calculated on the quantity of HNO_3 required. After adding all the mixed acid, the temperature is raised to 35-40°C and the nitrator contents are stirred for 2 hr. A sample taken from the nitrator should have a density of 1.155-1.160 g/cm^3.

The stirrer is then stopped and the contents allowed to settle for 2 hr. The waste acid (the lower layer) containing less than 0.2% HNO_3(sp. gr. = 1.60-1.61) is transferred to a storage vessel.

The oil is run into a washing tank where it is mixed with 100 1. of a 10% NaOH solution. The aqueous alkaline solution becomes dark red owing to the presence of sodium salts of mono- and di-nitrocresols.

The aqueous layer is separated and the oil washed with water until alkali free when tested with phenolphthalein. The oil is steamed to remove un-nitrated toluene and aliphatic compounds. Distillation is continued until the oil coming over sinks in water. The distillate is collected and fractionated once or twice a year. It contains ca. 20% of nitrotoluenes.

The steamed oil is dried in a drier of 25 m^3 capacity under reduced pressure (40 mm Hg) until a sample dissolves completely in an equal volume of 95% sulphuric acid.

To obtain 100 kg of nitrotoluene require

toluene	69 kg
mixed acid	150 kg
sodium hydroxide solution (10%)	2.2 kg
electricity	22 kWh
steam	930 kg

The washed and dried crude product should have a setting point not lower than 15.1%.

At Griesheim a continuous method of nitrating toluene to nitrotoluenes was also used. The nitration unit consisted of two nitrators connected by their bottom outlets, fed with mixed acid of the same composition as in the batch process.

The temperature in the two nitrators was:

I	25°C
II	45°C

The product and spent acid overflowed into a lead-lined separating tank. The nitration product contained l-2% of dinitrotoluene.

SEPARATION OF ISOMERS

The composition of the mononitrotoluenes prepared at Griesheim is:

62-63%	*ortho*
33-34%	*para*
3-4%	*meta*

Distillation of crude nitrotoluene. The still kettle is of 60 m^3 capacity, heated with 18.5 atm steam. The column has 40 plates, 8 m height, 2 m diameter.

55,000 1. of the crude, steam distilled and dried nitrotoluene are sucked into the still while heating up. Distillation begins under reduced pressure (15 mm Hg on the receiver and 120 mm Hg in the kettle) at a still temperature of 160°C. First runnings (ca. 200 1.) have a setting point lower than -10°C and contain nitrobenzene. As soon as the setting point reaches -10°C the second fraction (mainly *o*- nitrotoluene) is collected at a still base temperature of 180°C. The bulk of this faction has a setting point of -9.2°C.

When the contents of the still have a setting point of 40°C, the column is emptied into the base and distillation is continued without the column, at the still base temperature 185°C. This third fraction (mainly p-nitrotoluene) has a setting point of 40°C. The residue is tar.

Further purification is carried out by crystallization.

Crystallization of *p*- nitrotoluene. 8000 1. of crude molten *p*- nitrotoluene are charged into a tubular crystallizer, cooled to 39-40°C and this temperature is maintained for 24 hr. Then the whole is cooled to 18°C for 24 hr and the crystallizer is opened. The mother liquor is collected and the crystalline contents heated slowly to 50°C. The oil that was drawn off is collected separately and when it reaches

a setting point of 49°C, the pure p-nitrotoluene (s.p. 51°C) remaining in the crystallizer is melted out, dried and flaked. The mother liquor is distilled, and the oil collected during the heating up process is put back into the crystallizer.

Distillation of the mother liquor. 10,000 kg of *p*- nitrotoluene mother liquor are sucked into a still of 10 m^3 capacity with a column of 40 plates, of 8 m height and 1 m diameter. Distillation conditions are the same as in the distillation of crude nitrotoluene.

The first fraction (ca. 1500 kg) consists of crude *o*- nitrotoluene (70-80% *o*- and 20-30% *m*- isomer). The distillate has a setting point of ca. - 15°C. It drops to -20°C and at this temperature the collection of a second fraction (ca. 4000 kg) starts. The setting point continues to fall to ca. -30°C and then rises to +5°C. The distillate contains *ca.* 50% *meta*-, the rest being mainly *ortho*- isomer.

When the setting point of still contents reaches 40°C the third fraction is distilled off without the column. This is crude *p*- nitrotoluene (4500 kg). It is purified by crystallization as above.

Pure *m*- nitrotoluene is isolated by further distillation.

Continuous vacuum distillation of mononitrotoluene

The following modem continuous distillation unit is described by Vorontsov [20].

A neutralized, washed and dried crude mixture of nitrotoluenes passes from container (2) into the rectifying column (4), where *o*- nitrotoluene is distilled off. The column is 12 m high and 0.6 m diameter and is provided with boiler (3) still-head (5) and condenser (6). Before entering the column, the crude material passes through the lower part of the still-head, the expansion vessel (20) and a flowmeter which regulates the rate of supply of the liquid.

Steam supplied for heating the column (through a coil) has a pressure of 18-20 atm. It is fed through the boiler (3) and regulating valve (22). A constant level in the boiler is maintained by means of regulator (25). The vapours are partially condensed in the still-head (5), cooled by water flowing from (1). The same water is used to cool the condensers of both columns. The flow of water is regulated by means of valves (29) and (27).

The condensed distillate (pure *o*- nitrotoluene) flows partly back to the column but mostly down through (19) and the pump (14) transfers it into a storage tank. The vapours passing from the still-head (also o-nitrotoluene) are condensed in (6). From here they pass through (18) and pump (13) into a storage tank. If the condensed distillate is not of sufficient purity, it is sent back to the container (2) and subjected to a second distillation.

A mixture of *m*- and *p*- nitrotoluene which leaves the lower part of the column passes through the pump (15) into a second column (8). A part of it returns to column (4) (to avoid a fall of the level there in it). If, due to any disturbance of the process, the product flowing from the lower part of the column contains *o*- nitrotoluene, it is fed to (2) through pump (15) and rectified again.

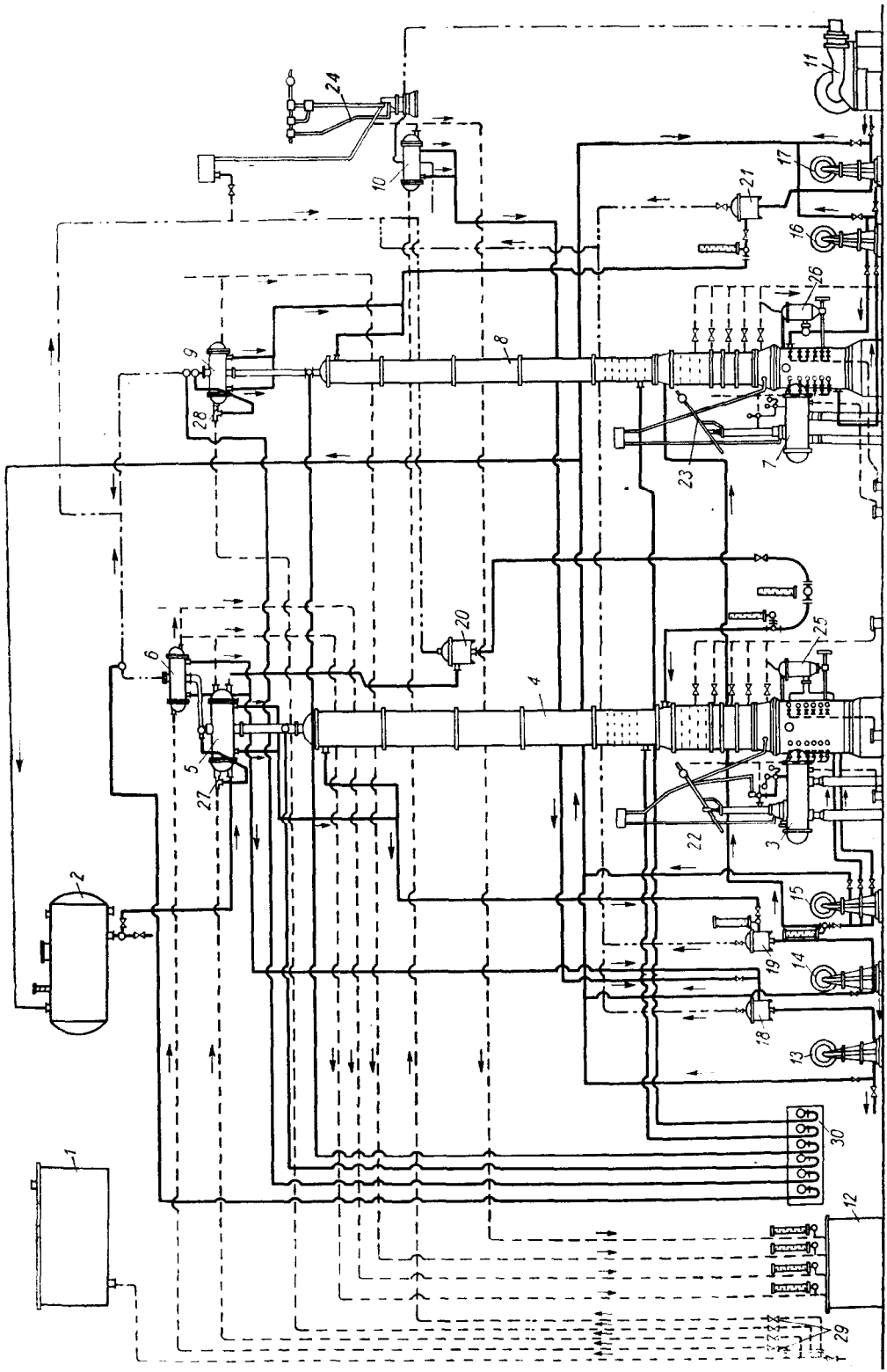


FIG. 58. Continuous distillation of nitrotoluene (Vorontsov 20])

Column (8) is 12 m high and 0.35 m in diameter. Here *m*- nitrotoluene is distilled off. *p*- Isomer flows to the lower part of the column. The column is heated through valve (23) and boiler (7) by means of a coil. The vapours leaving the column are condensed in (9) and cooled with water passing through (28).

Most of the condensed vapour returns to the column, and the rest flows down through (21) via a flowmeter and the pump (17) to a storage tank. Samples are taken through the valves near the pump and the setting point of the product is determined.

p- Nitrotoluene which falls into the lower part of the second column is transferred through the pump (16) to a crystallizer. Some of the *p*- nitrotoluene returns through (26) to the column if the level in the column is too low. Thermometers (30) serve to control the process.

TABLE 53
SPECIFICATION FOR *O*- NITROTOLUENE (AFTER U.S.S.R. DATA, GORST [2])

	I grade	II grade
Appearance	Clear oily liquid of a light yellow to light brown colour	
Boiling range not less than 90 vol. % at 760 mm Hg pressure should distil between	218-223°C	217-223.5°C
Dinitrotoluene	none	
Hydrocarbons	below 0.1%	below 0.1%
p- Nitrotoluene	below 1%	below 2%
Moisture	below 0.1%	below 0.1%

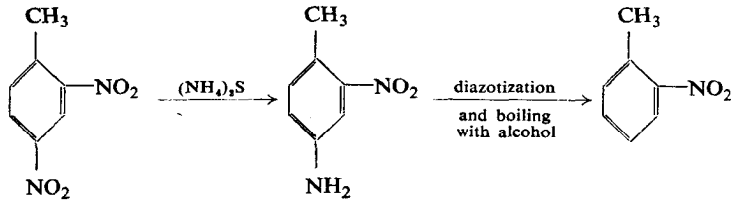
TABLE 54
SPECIFICATION FOR P-NITROTOLUENE (AFTER U.S.S.R. DATA, GORST [2])

	I grade	II grade
Appearance	light grey to light yellow crystals	
Freezing point, not below	50°C	49°C
Dinitrotoluene	none	
Hydrocarbons	none	
Moisture	below 1%	
Toluene insoluble substances	below 0.1%	

Distillation in both columns occurs in the upper parts under a reduced pressure of 10 mm Hg. The vacuum pipe is connected with condensers (6) and (9) and expansion vessels (18) (19) (20) (21) and with the regulatingvalve (24). The vapours which penetrate into the vacuum pipe, are condensed in condenser (10) and flow down through (18). All pipes for *m*- and *p*- nitrotoluene should be insulated to avoid solidification of the products.

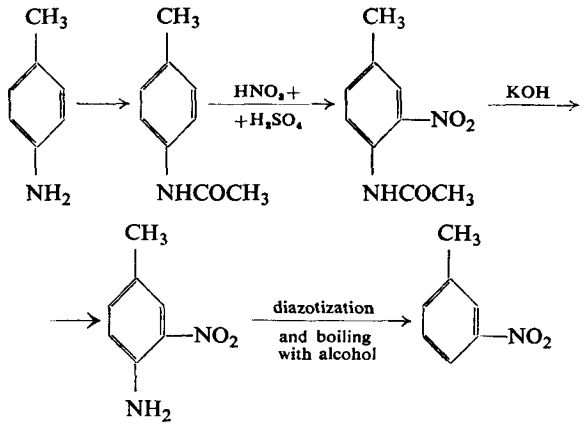
Preparation of pure isomers. Since the isolation of high purity *o*- and *m*- isomers from a mixture obtained by direct nitration is rather difficult, the very pure substances have been obtained by indirect methods.

o- Nitrotoluene was obtained by Beilstein and Kuhlberg [21] from 2,4-dinitrotoluene :



(4)

m- Nitrotoluene has also been obtained from *p*- toluidine by the same workers:

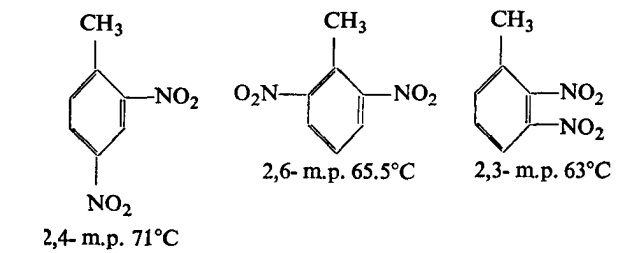


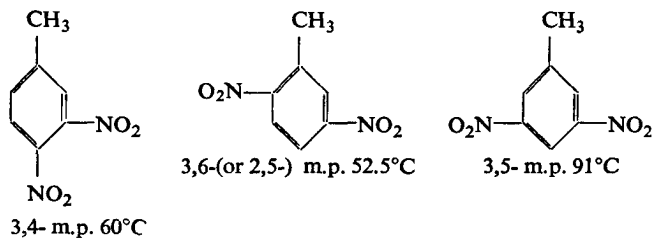
(5)

The fairly pure *p*- isomer may be isolated from a mixture of nitrotoluenes by freezing and repeated crystallization.

DINITROTOLUENES

Six isomeric dinitro derivatives of toluene are known:





PHYSICAL PROPERTIES

All the isomers are pale yellow, crystalline products. The composition of the eutectic formed by 2,4-dinitrotoluene with α– trinitrotoluene is given in Table 66 (p. 295).

The solubility of technical DNT (the mixture of isomers) in sulphuric acid was given by Orlova [2a] (Table 55).

TABLE 55

SOLUBILITY OF TECHNICAL DNT IN SULPHURIC ACID

Concentration % H_2SO_4	Solubility: g of DNT in 100 g of the acid at temperatures °C					
	20	40	50	70	100	120
80.0	1.2	-	2.5	3.8		
83.6	-	3.6	4.7	6.3	6.4	6.5
88.7	6.1	10.0	12.8			17.4
90.0	8.5	-	16.8	20.0	-	-
93.0	-	26.4	33.8	58.3	82.4	66.6
99.8	-	72.6	14.4	1121	1360	-

THERMOCHEMICAL PROPERTIES

According to Bichel [22] the heat of formation of 2,4-dinitrotoluene is 7.7 kcal/mole; Koehler [23] has reported it to be 5.9 kcal/mole.

Garner and Abernethy [3] give the following values for the heats of combustion and heats of formation of the isomers (see also Fig. 50, p. 261).

The same authors have calculated the heat of nitration of mono- to di-nitrotoluene.

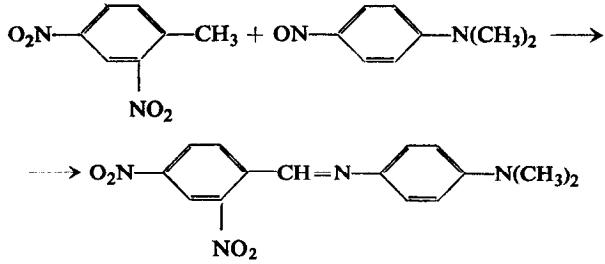
TABLB 56

HEATS OF COMBUSTION AND HEATS OF FORMATION OF THE DINITROTOLUENE ISOMERS

Dinitrotoluene isomer	Heat of combustion (at constant volume) k&/mole	Heat of formation kcal/mole
2,4-Dinitrotoluene	853.7	+31.3
2,6-Dinitrotoluene	855.2	+29.6
2.3-Dinitrotoluene	860.5	+24.3
2,5-Dinitrotoluene	856.1	+28.7
3,4-Dinitrotoluene	860.8	+24.0
3,5-Dinitrotoluene	853.9	+30.9

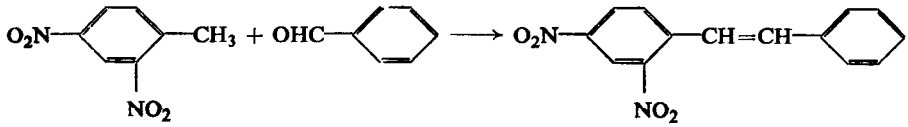
CHEMICAL PROPERTIES

The methyl group in dinitrotoluenes is particularly reactive due to the presence of two nitro groups. Thus it readily undergoes such reactions as for example with *p*- nitrosodimethylaniline to form an anil:



(6)

or with benzaldehyde, in the presence of piperidine, to form a stilbene derivative:



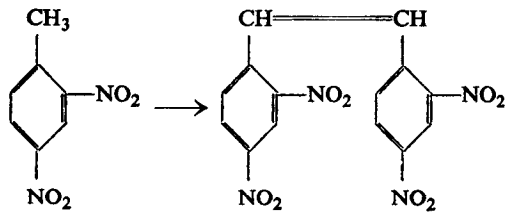
(7)

TABLE 51

HEAT OF NITRATION OF MONO- TO DINITROTOLUENE (CF. FIG. 50)

Starting product	Nitration product	Reaction heat kcal/mole
o- Nitrotoluene	2.4-Dinitrotoluene	+29.7
o- Nitrotoluene	2,6-Dinitrotoluene	+28.2
p- Nitrotoluene	2,4-Dinitrotoluene	+21.3
m- Nitrotoluene	2,3-Dinitrotoluene	+18.8
m- Nitrotoluene	3,4-Dinitrotoluene	+18.5
m- Nitrotoluene	3,6-Dinitrotoluene	+23.2
m- Nitrotoluene	3,5-Dinitrotoluene	+25.4

Under the influence of alkalis it forms a stilbene derivative, especially easily in the presence of oxidizing agents (air oxygen, NaOCl):



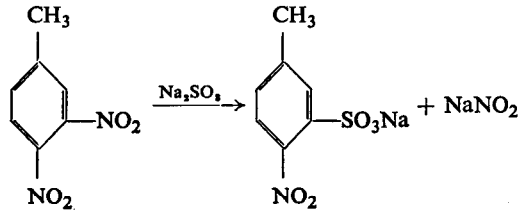
(8)

The ease of these reactions can be explained in terms of the hyperconjugation of toluene accentuated by the influence of the nitro groups.

With lead in the presence of dilute nitric acid, 2,4-dinitrotoluene forms inflammable organo-metallic products (for further details see p. 306, Kovache and Thibon's work).

An acetone solution of 2,4-dinitrotoluene treated with a 10 per cent solution of KOH gives a blue colour (the Janovsky reaction), unlike the 2,6-isomer, which gives no colour at all.

Dinitrotoluenes derived from *m*- nitrotoluene react with sodium sulphite to form sodium salts of nitrosulphonic acid, e.g.:



(9)

The reaction occurs with more difficulty than the corresponding one with the unsymmetrical trinitrotoluenes and requires a higher temperature or more concentrated solutions of sodium sulphite. The reaction of "sulphitation" of dinitrotoluene may be used in practice for removing m-nitrotoluene derivatives from mixtures of dinitro-isomers. Thus the sulphitation of trinitrotoluene becomes unnecessary.

Dinitrotoluenes are able to form molecular compounds with condensed ring aromatic hydrocarbons and also with amines. According to Kremann [24], 3,5-dinitrotoluene is the most ready to form such compounds, while the others can be ranged according to their decreasing ability to do so in the following order: 2,4-, 2,6-, 3,4-.

Here is a list of some of the molecular compounds obtained by Kremann:

	Dinitrotoluene isomer	Molecular proportion	m. p., °C
with: naphthalene	2.4-	1:1	59
naphthalene	3,5-	1:1	63.2
acenaphthene	2,4-	1:1	61
acenaphthene	3,5-	1:1	94
aniline	3,5-	1:1	46.5
p- toluidine	3,5-	1:1	non uniform
β -naphthylamine	3,5-	1:1	53
α -naphthylamine	2,4-	1:l	107.8
α -naphthylamine	3,5-	1:1	62

Aniline, *p*- toluidine and β -naphthylamine do not combine with 2,4-dinitrotoluene.

TOXICITY

Dinitrotoluene is regarded as a poisonous substance, but in a less degree than dinitrobenzene. If has been suggested that poisoning by dinitrotoluene should be ascribed to the impurities present in it, mostly dinitrobenzene.

PREPARATION OF DINITROTOLUENES

The principal reaction products in the nitration of toluene are the isomers: 2,4- formed from *o*- and *p*- nitrotoluenes, and 2,6- formed from *o*- nitrotoluene. From *m*- nitrotoluene the 2.3-, 3,4- and 3,6-isomers are formed. The possibility of the formation of the 3,5-isomer in the direct nitration of *m*- nitrotoluene has not been definitely proved.

Dinitrotoluene (2,4-) was first obtained by Beilstein and Kuhlberg [21] in 1870. However, it may be that "dinitrobenzene", m.p. 71°C obtained in 1841 by St. Claire Deville [25] by the nitration of "nitrobenzene" prepared from light oil, was in fact dinitrotoluene. As Rosensriel [26] found in 1872 *p*- nitrotoluene yields only one product of dinitration, viz. the 2,4-isomer, while *o*- nitrotoluene gives in addition another isomer, the structure of which he did not determine.

The first indication of the existence of the other dinitrotoluene isomers can be found in the Limpricht's work [27]. He was able to isolate from the nitration products the 3,6-isomer, besides the 2,4- and 2,6-isomers. In 1903 Zaloziecki [28] nitrated the aromatic fraction of Galicia oil and isolated the 2,4- and 3,6-nitrotoluenes.

Beilstein and Kuhlberg nitrated the *m*- nitrotoluene in 1873 and obtained the 3,4-isomer.

The data were confirmed by Häussermann and Grell [29] in 1894. They stated that besides the isomers already mentioned, the 3,5-isomer was also isolated. Several authors questioned the presence of the latter isomer in the nitration products. For example, Sirks [30] reporttd that nitration of *m*- nitrotoluene resulted in the formation of the 3,4-, 2,3-, and 3,6-isomers, but not the 3,5-isomer.

Gibson, Duckham and Fairbairn [13] have carried out more detailed studies, in which they established that the following proportions of isomers are formed in the nitration of various mononitrotoluenes (Table 58):

TABLE 58

NITRATION OF NITROTOLUENE ISOMERS

Substance being nitrated	Dinitrotoluene isomers, content %				
	2,4-	2,6-	3,4-	2,3-	3.6-
o- Nitrotoluene	67	33	-		-
p- Nitrotoluene	100	-	-	-	-
m- Nitrotoluene	-	-	55	25	20

De Beule [31] carried out the most extensive study of nitration of *m*- nitrotoluene. He found the product was composed of 54.6% of 3,4-dinitrotoluene, 30.6% of 2,3-dinitrotoluene, 13.0% of 2,5-dinitrotoluene, and 1.8% of 2,5-dinitrotoluene. Thus he confirmed the formation of 3,5-isomer.

The crude dinitrotoluene consists (according to de Beule) of the following isomers :

2.4-dinitrotoluene	76.1%
2,6-dinitrotoluene	19.8%
3,4-dinitrotoluene	2.25%
2,3-dinitrotoluene	1.23%
2,5-dinitrotoluene	0.54%
3,5-dinitrotoluene	0.08%

Recently Kobe, Skinner and Prindle [32] reported their extensive studies on the nitration of *o*- and *p*- nitrotoluenes to dinitrotoluene. They concluded that the most favourable parameters of the nitration of *o*- and *p*- nitrotoluenes differed somewhat from each other. Thus the concentration of mixtures for nitrating *o*- nitrotoluene might vary within a wider range, especially with regard to the quantity of sulphuric acid. Also, lower temperatures may be applied for the nitration of *o*- nitrotoluene.

According to these authors, the following conditions are the most favourable in the nitration of 200 g of nitrotoluenes:

	o- Nitrotoluene	*p*- Nitrotoluene
Nitric acid weight	theoretical	theoretical
Sulphuric acid weight	250-350 g	350 g
Sulphuric acid concentration	90%	90%
Temperature	50°C	65°C
Reaction time	15-20 min	15-20 min.
Yield	100%	98%

Figures 59, 60 and 61 show the influence of temperature and concentration of sulphuric acid on the yield of dinitrotoluene using *o*- and *p*- nitrotoluene as starting materials.

Gorst and Trufanova [32a] stated that the nitration of *p*- nitrotoluene proceeds with a noticeable rate at 70°C when the nitrating mixture has the factor $\Phi = 72\%$. Increase of Φ to 79.84% increases the rate of the reaction five times (Table 59 and Fig. 62).

TABLE 59

Φ, %	71.83	74.07	75.92	77.77	79.84
Rate, $-\frac{\text{mole}}{\text{l. min}} \times 10^{-2}$	16.3	42.9	60.6	74.4	85.0
Quantity of nitrated mononitrotoluenes, %	17.8	46.5	65.1	78.7	88.8

Increased rate of stirring also produces an increase in the rate of nitration. Orlova [32a] gives a diagram (Fig. 63) related to the nitration of *p*- nitrotoluene with nitrating mixture containing 4% HNO_3, 74% H_2SO_4 and 23% H_2O at 70°C.

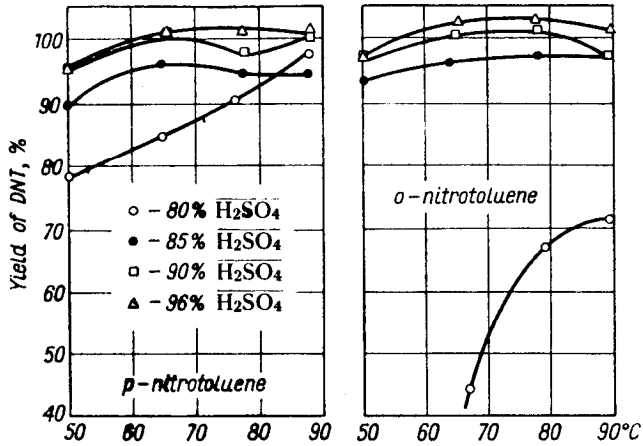


FIG. 59. Influence of temperature on the yield of DNT. Nitration of *o*- and *p*- nitrotoluenes in nitrating mixtures with various concentrations of sulphuric acid (Kobe. Skier and Prindle ([32]).

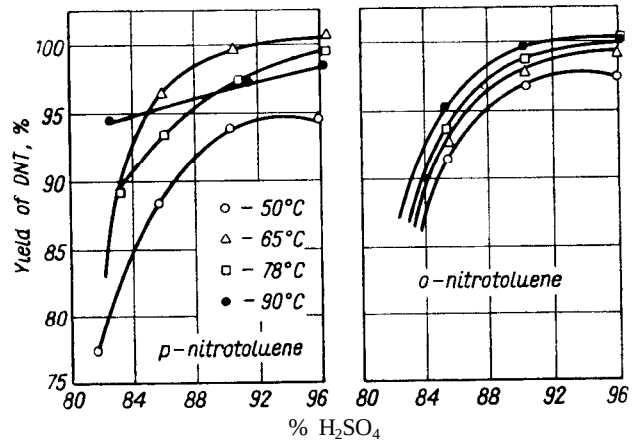


FIG. 60. Influence of the concentration of sulphuric acid on the yield of DNT. Nitration of *o*- and *p*- nitrotoluenes (Kobe, Skinner and Prindle ([32]).

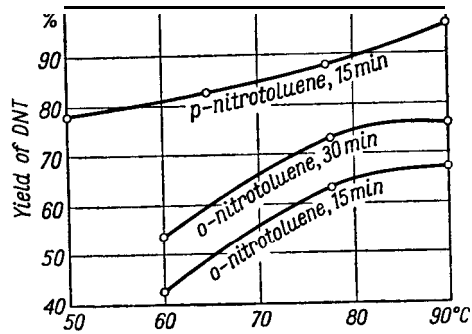


FIG. 61. influence of temperature and time on the yield of DNT. Nitration of *o*- and *p*- nitrotoluenes (Kobe, Skinner and Prindle ([32]).

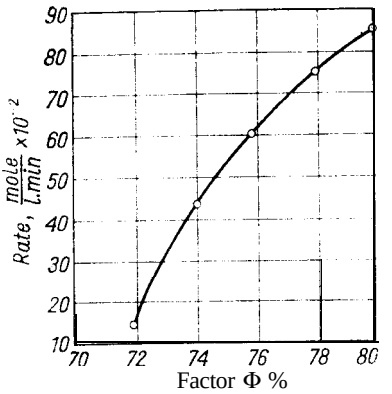


FIG. 62. Influence of the factor Φ (nitrating activity) on the rate of nitration of *p*- nitrotoluene at 70°C (Gorst and Trufanova [32a]).

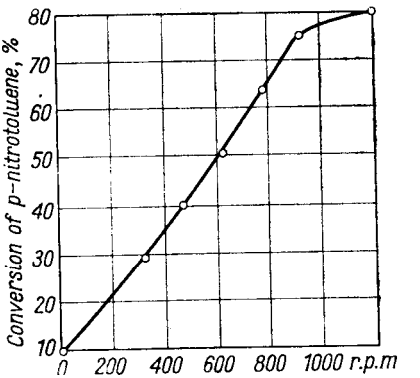


FIG. 63. Influence of the intensity of stirring on the rate of nitration of *p*-nitrotoluene (Orlova ([2a]).

INDUSTRIAL METHODS OF PREPARATION OF DINITROTOLUENE

In industrial practice, mononitrotoluene is nitrated with a mixture of composition ranging:

HNO_3 28-34% H_2SO_4 60-64% H_2O 5-8%

The manufacture of dinitrotoluene at the Griesheim factory (I. G. Farbenindustrie), described below, may serve as an example.

4000 kg of *o*- and *p*- nitrotoluene (the latter should be melted) is run into the nitrator at a temperature of 25°C and 55°C respectively. Then 5500 kg of mixed acid of composition :

HNO_3 33.5% H_2SO_4 60.7% H_2O 5.8%

are run in, so that the temperature in the case of *p*- nitrotoluene follows the curve (Fig. 64).

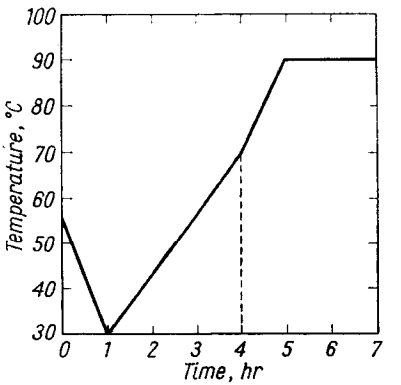


FIG 64. Temperature change during the nitration of *p*- nitrotoluene (BIOS 1144).

When all the acid has been added over a period of 4 hr, heat is applied to raise the temperature to 90°C which is held for a further 2 hr. A test sample is steam distilled and no smell of nitrotoluene should be present in the distillate.

If mononitrotoluene is detected, a further 50 kg of mixed acid is added and heating is continued at 90°C for a further half an hour. The contents of the nitrator are diluted with 350-400 1. of water to give a waste acid of 73% H_2SO_4 containing ca. 0.1% HNO_2.

After settling, the waste acid is run into the washing tank (a lead-lined vessel of 12 m^3 capacity) where the acid from three or four previous nitrations is collected and washed with sufficient crude nitrotoluene and *o*- nitrotoluene to form one batch for nitration to dinitrotoluene. After settling, the washed waste acid is collected in the acid storage tank. The nitrotoluene is pumped or blown to the nitrator.

In the washing tank, a stainless steel vessel of 12 m^3 capacity, dinitrotoluene is washed with 4000 1. hot water and the wash water is blown to drain. 4000 1. of hot water are then run in and while stirring, sufficient solid NaOH is added to obtain a neutral reaction. The wash liquor is discarded and the product is washed with water to remove excess NaOH.

The molten dinitrotoluene is run into the vacuum dryer, and heated at 120°C at a pressure of 15 mm Hg for 5 hr. It is tested for moisture by heating a small amount in a test-tube and looked for condensation on the side of the tube. The material is made up into solid blocks or flakes (flaking as for TNT, p. 379).

Dinitrotoluene, prepared by nitrating *p*- nitrotoluene, and free from *m*- nitrotoluene, should not melt below 64.5°C. It should contain not less than 96% of 2,4-dinitrotoluene.

The specification, according to U.S.S.R. data (Gorst [2]) given below (Table 60) is for commercial dinitrotoluene, i.e. for the product prepared from a mixture of nitrotoluenes.

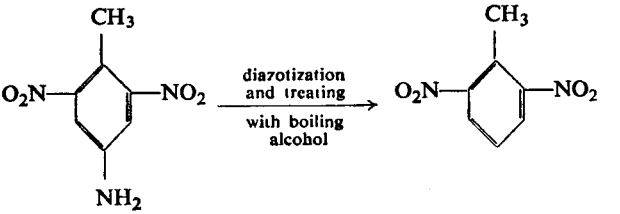
TABLE 60

SPECIFICATION FOR COMMERCIAL DINITROTOLUENE

Appearance	crystalline yellow product, free from visible impurities
Moisture content	below 1.5%
Mononitrotoluene con tent	below 1.0%
Benzene insoluble substances	below 0.1%
Ash	below 0.1%
Sand in the ash	not more than 0.05%
Acidity	not more than 0.005% as H_2SO_4
Melting point of the dry product	not below 50°C and not higher than 55°C
Product used for nitration to TNT	below 76°C

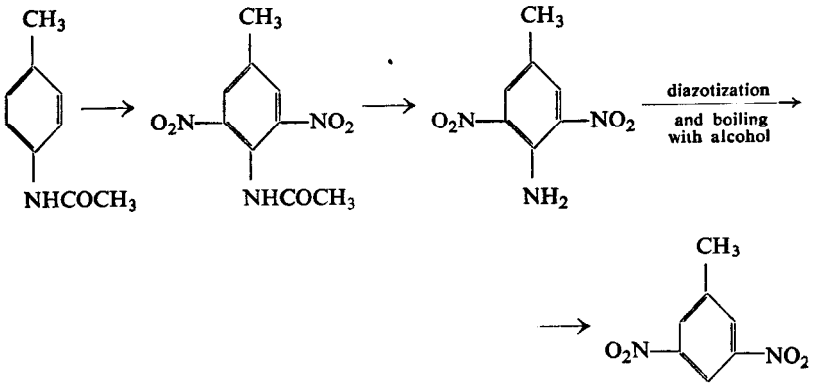
PREPARATION OF PURE ISOMERS

Pure 2,4-dinitrotoluene may be obtained by the direct nitration of *p*- nitrotoluene. 2,6-Dinitrotoluene of high purity may be obtained from 2,6-dinitrotoluidine:



(10)

3,5-Dinitrotoluene, difficult to obtain by direct nitration, may be prepared in the following way:



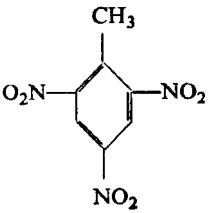
(11)

3,6 (or 2,5-)-Dinitrotoluene was obtained by Page and Heasman [33] by the oxidation of 5-nitro-o-toluidine with Caro's acid.

All other isomers are prepared by nitration of *m*- nitrotoluene, followed by fractional crystallization of the product.

α– TRINITROTOLUENE (TNT)

The commercial product for military purposes consists of α– trinitrotoluene (2,4,6-isomer) of high purity.



In the explosives industry it is known under various names: Tolite (France); Tri, Trotyl, Tutol, Trinol. Füllpulver 1902 - abbreviation Fp02 (Germany); Tritolo (Italy); Trotyl and TNT (Poland); Trillit, Tolita (Spain); TNT (United Kingdom and U. S. A.); Tol, Trotil, TNT (U. S. S. R.).

Trinitrotoluene was first mentioned in 1863. It was obtained by Wilbrand [34], who treated toluene with a mixture of nitric and sulphuric acids at a temperature

"close to boiling point". Later Beilstein and Kuhlberg [21], in a paper published in 1870, which describes the most extensive work on the nitration of aromatic hydrocarbons carried out in the last century, gave details of the nitration of *o*-, *m*-, and *p*- toluencs to trinitro derivatives. Besides α– trinitrotoluene they also isolated the γ– isomer.

The β– and γ– isomers were obtained by Hepp [35] in 1882. The constitution of the α -isomer was determined by Claus and Becker [36] in 1883, and that of the β– and γ by Will [37] in 1914 (see also pp. 311 and 336, 337).

PHYSICAL PROPERTIES

α– Trinitrotoluene crystallizes in the form of small columns or needles.

According to Artini [38], α– trinitrotoluene forms monoclinic crystals, of the prismatic class, with the axial ratio ***a:b:c*** = 1.64047:1:0.61936.

Melting point and purity. The melting point of α– trinitrotoluene has been determined by several workers as 80.6°C, 80.65°C, 80.8-80.85°C, 80.66°C. The value of 80.65°C is generally accepted, and usually determined as setting point.

Three grades of commercial TNT are usually prepared, the main difference between them consisting in their purity and hence in the melting point. The standards for TNT, accepted in several countries, differ somewhat.

Polish standards of 1930 cover the requirements for the following grades of TNT:

I. m.p. 80.3°C
II. m.p. 80.0°C
III. m.p. 76.0°C

U.S.S.R. standards (Gorst [2]) specify the following grades of TNT:

I. military TNT	m.p. 80.2°C
II. TNT for the manufacture of ammonites:	
(a) sulphited (for permissible explosives)	m.p. 80.0°C
(b) washed only	m.p. 77.5°C
III. waste TNT	m.p. 75.0°C

In Great Britain, during World War I the following minimum melting points of TNT were specified:

I. m.p. 80.0°C
II. m.p. 79.5°C
III. m.p. 76.0°C

In the U. S. A. two grades of TNT have been introduced on the market:

I. m.p. 80.2°C
IL m.p. 76.0°C

According to Gorst [2], the U. S. S. R. requirements to crystallized TNT are as follows.

(1) Light yellow crystalline powder without any visible foreign inclusion. Should pass through the 3 mm size sieve.
(2) Setting temperature not below 80.2°C

(3) Water and volatile matters-no more than 0.075%.
(4) Acidity (as H_2SO_4) - no more than 0.01%.
(5) Substances insoluble in benzene - no more than 0.15%.
(6) Content of ash - no more than 0.1%.
(7) Content of oily products - lower than in the standard substance.

The low melting point of α– trinitrotoluene is due mainly to the presence of trinitrotoluene isomers, and to a lesser degree, to the presence of other impurities, such as trinitrobenzene, trinitrocresol, dinitrotoluene.

Since the trinitrotoluene isomers are formed as a result of the nitration of *m*- nitrotoluene, W. W. Jones and Russel [9] undertook the task of determining to what extent the presence of *m*- nitrotoluene in mononitrotoluene lowers the melting point of α– nitrotoluene. The authors nitrated mixtures of *m*- and *p*- nitrotoluenes (Table 61).

TABLE 61

RELATIONSHIP BETWEEN LOWERING THE MELTING POINT OF TNT AND THE CONTENT OF *m*- NITROTOLUENE IN MONONITROTOLUENE

m- Nitrotoluene content, % / Melting point °C	0	2.11	3.22	4.58	5.75
Found experimentally	80.78	79.87	79.26	78.70	78.13
Calculated from formula (12)	80.80	79.82	79.30	78.67	78.13

Pure 2,4-dinitrotoluene was also nitrated for comparison and, as a result trinitrotoluene melting at 80.80°C was obtained.

Jones and Russel propose the following empirical formula for the calculation of the melting point of TNT, depending on the *m*- nitrotoluene content in mononitrotoluene:

$$\text{m. p.} = 80.80\text{-}0.465c \qquad (12)$$

where c is the percentage of *m*- nitrotoluene.

Solubility. *a*- Trinitrotoluene is rather insoluble in water. It dissolves in concentrated sulphuric or nitric acids and is precipitated from the solutions on adding water.

The solubility data for α– trinitrotoluene in sulphuric acid of various concentrations are tabulated in Table 62 (Belenkii [39]).

TNT dissolves with difficulty in nitrating mixtures. Its solubility may however be fairly high when the content of HNO_3 in the nitrating mixture falls to a few per cent, as in waste acid.

Solubility data for α– trinitrotoluene in various mixtures at 20°, 50° and 70°C are shown in Table 63.

The solubility of α– trinitrotoluene in nitric acid is high even when the acid is relatively dilute (Table 64). This property is sometimes used in industry to crystallize TNT.

α– Trinitrotoluene dissolves readily in organic solvents, such as acetone, benzene, and toluene. The corresponding data, after Taylor and Rinkenbach [40], are presented in Table 65.

TABLE 62

SOLUBILITY OF a- TRINITROTOLUENE IN SULPHURIC ACID (IN %)

Concentration H_2SO_4, % / Temperature °C	70	75	80	85	90	95	100
0	-	0.3	0.4	0.6	2.0	3.5	13.0
10	-	0.3	0.45	0.75	2.2	4.0	13.5
20		0.3	0.50	0.85	2.5	4.8	15.0
25	.-	0.32	0.55	0.95	2.6	5.2	15.5
30	--	0.35	0.60	1.0	2.7	6.0	16.5
40	0.2	0.4	0.65	1.3	3.0	7.0	18.0
50	0.2	0.45	0.70	1.7	3.5	8.5	21.0
60	0.22	0.50	1.0	2.3	5.2	11.0	24.8
70	0.35	0.7	1.6	3.3	7.0	13.5	29.0
80	0.6	1.3	2.4	4.8	10.0	18.0	26.5

TABLE 63

SOLUBILITY OF α– TRINITROTOLUENE IN ACID MIXTURES

Composition of the mixture, %			Solubility, %		
H_2SO_4	HNO_3	H_2O	20°C	at 50°C	at 70°C
60	0	40	0.20	0.52	0.70
80	0	20	0.59	1.25	2.07
90	0	10	2.55	4.70	7.63
60	1	39	0.22	0.41	0.62
80	1	19	0.55	1.08	1.68
90	1	9	1.85	4.35	7.49
60	5	35	0.25	0.55	1.23
80	5	15	0.73	1.48	1.85
90	5	5	1.76	4.49	7.53

100 parts of carbon disulphide dissolve 0.4 parts of α– trinitrotoluene at 15°C and 2.7 parts at 46°C.

α– Trinitrotoluene forms eutectics with higher nitrated aromatic compounds and with nitric esters. Some of them have a considerable practical importance such as the mixtures of α– trinitrotoluene with cyclonite, pentaerythritol tetranitrate, tetryl etc. (Vol. IV).

TABLE 64

SOLUBILITY OF α– TRINITROTOLUENE IN NITRIC ACID (ACCORDING TO ORLOVA [2a])

Concentration % HNO_3	Temperature °C	Solubility in g of α– trinitrotoluene in 100 g of nitric acid
78.2	48	100
	53	150
	56	200
	59	250
	61	300
80.4	44	100
	50	150
	54	200
	56	250
82.5	38	100
	46	150
	50	200
	54	250
	56	300
84.7	33	100
	41	150
	46	200
	54	300
91.8	26	150
	34	200
	45	300
	55	500
97	34	235
	47	376
	52	458
	57	650
	61	830

TABLE 65

SOLUBILITY OF α– TRINITROTOLUENE (g/100 g SOLVENT)

Temperature	Water	CCl_4	Benzene	Toluene	Acetone	Ethanol 95%	$CHCl_3$	Ether
0	**0.0100**	**0.20**	**13**	**28**	**57**	**0.65**	**6**	**1.73**
5	**0.0105**	**0.25**	**24**	**32**	**66**	**0.75**	**8.5**	**2.08**
10	**0.0110**	**0.40**	**36**	**38**	**78**	**0.85**	**11**	**2.45**
15	**0.0120**	**0.50**	**50**	**45**	**92**	**1.07**	**15**	**2.85**

Table 65 (continued)

Temperature, °C	Water	CCl_4	Benzene	Toluene	Acetone	Ethanol 95%	$CHCl_3$	Ether
20	0.0130	0.65	67	55	109	1.23	19	3.29
25	0.0150	0.82	88	67	132	1.48	25	3.80
30	0.0175	1.01	113	84	156	1.80	32.5	4.56
35	0.0225	1.32	144	104	187	2.27	45	-
40	0.0285	1.75	180	130	228	2.92	66	
45	0.0360	2.37	225	163	279	3.70	101	
50	0.0475	3.23	284	208	346	4.61	150	-
55	0.0570	4.55	361	272	449	6.08	218	
60	0.0675	6.90	478	367	600	8.30	302	
65	0.0775	11.40	665	525	843	11.40	442	-
70	0.0875	17.35	1024	826	1350	15.15		
75	0.0975	24.35	2028	1685	2678	19.50		
80	0.1075	-	-.	-	-	-	-	-
85	0.1175	-	-	-	-	_	-	
90	0.1275	-	-	-	-	-.	-	
95	0.1375	-	-	-		-	-	-
100	0.1475	-	-	-	-	-	-	-

TABLE 66

EUTECTICS WITH *a*- TRINITROTOLUENE

The second component	Weight % of TNT	m.p., °C	Author
Cyclonite	97.5	78.6	T. Urbanski and Rabek-Gawroriska [41]
m- Dinitrobenzene	54.5	51	Hrynakowski and Kapuscinski [42]
1,8-Dinitronaphthalene	82	73.4	Khaibashev and Gromova [43]
2,4-Dinitrotoluene	50	45.6	Bell and Herty [44]
	46	45	Langenscheidt [45]
	48	45.8	Hrynakowski and KapuScitMi [421
	41.4	46.3	Burkhardt [150]
Hexyl	88	78.2	Giua [46]
Nitrobenzene	7	2.0	Hammick, Andrews and Hampson [47]
Nitroglycerine	17.6	7.0	Tamburrini [48]
	15	6.4	Lehmstedt 1491
	17.1	6.3	Hackel [50]
o- Nitrotoluene	16	-15.6	Bell, Gordon, Spry and White [51]
	19.5	-9.7	
p- Nitrotoluene	42	34	Bell and Herty [44]
Pentaerythritol tetranitratc	87	76.1	T. Urbanski [52]
Picric acid	65	59.8	Taylor and Rinkenbach [40]
	66	55	Giua [46]
	68	59	Hrynakowski and Kapu&ciiki [42]
	66.4	63.3	Burkhardt [151]
Tetryl	57.9	58.3	Jefremov and Tikhomirova [53]
Trinitro-m-cresol	43.3	41.3	Jefremov [54]
Trinitro-m-xylene	92	75	Bell and Sawyer [55]; Jefremov and Tikhomirova [53]

Some of the eutectic compositions are given in Table 66.

A number of tertnery eutectics containing α– trinitrotoluene have also heen examined, e.g. *a*- trinitrotoluene, 2,4-dinitrotoluene, *p*- nitrotoluene, m. p. 16.7°C (Bell and Herty [44]); α– trinitrotoluene, *p*- nitrotoluene, *o*- nitrotoluene, m. p. -19.5°C (Bell and Spry [56]) ; α– trinitrotoluene, β– trinitrotoluene, γ– trinitrotoluene, m. p. 44.4°C (Gibson, Duckham and Fairbairn [13]) ; α– trinitrotoluene, 2,4-dinitrotoluene, *m*- dinitrobenzene, m.p. 29°C (Hrynakowski and Kapuscinski [42]).

Hygroscopicity. α– Trinitrotoluene is practically non-hygroscopic. At room temperature, when exposed to air, saturated with water, it absorbs only 0.05% of water.

Specific gravity and density of loading. The specific gravity of solid α– trinitro toluene is 1.654-1.663 according to various authors, while that of the molten product is 1.467 at 82°C. The density of TNT, compressed under pressures varying from 1450 to 4350 kg/cm^2, is 1.54-1.62 g/cm^3 (Kast [57] 1907).

According to Dautriche [58], depending on the pressure applied, the following average density of loading can be obtained:

pressure, kg/cm^2	Mean density, g/cm^3
215	1.320
685	1.456
1375	1.558
2000	1.584
2750	1.599
3435	1.602
4125	1.610

The apparent weight of crystalline α– trinitrotoluene is 0.9.

If molten trinitrotoluene solidifies under pressure, a high specific gravity amounting to 1.62 may be obtained at a low pressure of about 5 kg/cm^2. Zanardi [59] obtained the following values :

Pressure, kg/cm^2	Mean density, g/cm^3
1	1.54
2	1.58
3	1.60
4	1.616
5	1.620

According to Kast [57] (1921), the specific gravity of α– trinitrotoluene, when allowed to solidify slowly after being melted is 1.57. When rapidly cooled with stirring, a product is obtained having a specific gravity of 1.59-1.61.

Plastic properties of TNT. In 1945 Jefremov and Khaibashev [60] found that at a temperature of 50°C and above, TNT exhibits the properties of a plastic material, as under pressure (e.g. 31.6 kg/mm^2) at 50°C it flows off through the holes in the vessel. At a temperature ranging from 0°C to 35°C TNT behaves as typical brittle material. At a temperature of 35-40°C (or at 45-47°C with TNT of high purity) a transition from the brittle to the plastic state can be observed.

Jefremov and Khaibashev [60] have also investigated melts of TNT with other nitro compounds. They observed deep minima on the isotherms of plastic flow of mixtures of TNT and picric acid, trinitroxylene or 1,8-dinitronaphthalene. corresponding to eutectic mixtures. Unlike those the corresponding curves for mixtures of TNT and 2,4-dinitrotoluene, *m*- dinitrobenzene, and tetryl, showed an additive character.

Crystallization. Very often it is necessary to obtain explosives (TNT among them) in readily precipitated form. Cave, Krotinger and McCaleb [61] developed a general method of crystallization which consists essentially in introducing the hot solution of a substance into cold diluting liquid or solid carbon dioxide.

Thus when a solution of α– trinitrotoluene in methanol is introduced into water, small and uniform crystals which are readily "pourable" are formed. Less uniform crystals of needle like form are obtained by pouring a methanol solution of α– trinitrotoluene into solid carbon dioxide. The results are given in Table 67.

TABLE 67

Methanol solution of TNT is poured into	Average dimensions of the crystals, μ	Limits of dimensions of the crystals, μ	Ratio of axes length/width
solid CO_2	29	3.5430	9.6
water	25	6-60	3.0

The rate of crystallization of TNT has been studied by Pelchowicz and Bergmann [62]. They found it decreased when various compounds were added, forming homogeneous melts with TNT, for example certain aromatic compounds, among others picric acid.

The elucidation of the influence of admixtures on the linear rate of crystallization of TNT has been the subject of more detailed studies by Gey, Dalbey and Van Dolah [63]. They found that some compounds, as for example 2,4,6-trinitrostilbene and a number of its derivatives (e.g. 3-nitro-, 4-nitro-2-chloro-, 2-methoxy-, 4-hydroxy-, 4-methoxy-), caused a very sharp fall of the rate of crystallization of TNT. For example, the addition of 1 mole % of 2,4,6-trinitrostilbene to TNT reduced its linear rate of crystallization at 74°C almost nine times: from 2.5 cm/min (pure TNT) to 0.29 cm/min.

Other compounds such as 2,4-dinitrotoluene, 2,4,6-trinitro-m-xylene, 2,4,5-trinitrotoluene, hexogen, only slightly decreased the rate of crystallization (e.g. the addition of 1 mole % of 2,4-dinitrotoluene and hexogen caused a decrease in rate of crystallization of TNT at 74°C from 2.5 cm/min to 1.89 and 1.78 cm/min respectively).

Boiling point and vapour pressures. Giua [64] reported in 1919 that trinitrotoluene may be boiled. According to this author, it can be distilled off at 210-212°C, under a reduced pressure of 10-12 mm Hg without any visible decomposition.

Belayev and Yuzefovich [65] found the boiling point of TNT at 2 mm Hg pressure to be 190°C and at 50 mm Hg 245-250°C; these values are consistent with those quoted above.

The authors have determined the boiling point of trinitrotoluene at normal pressure by extrapolation and found it to be 300±10°C. The direct determination of the boiling point, is of course impossible, since it is near to the initiation temperature of the substance.

A. J. B. Robertson [66] reported 345°C as the condensation temperature of trinitrotoluene vapours at 760 mm Hg, and 232°C at 30 mm Hg. Considering that the experimental conditions were difficult, it should be accepted that the results of all three workers are consistent. The value of 530°C, earlier determined by Menzies [67] by extrapolation of the results of vapour pressures measurements and heats of evaporation, is less probable.

Vapour pressures of trinitrotoluene have been determined by several authors. The first measurements were carried out by Verola [68] between 1911 and 1912. He found a value of 25 mm Hg at 183°C and soon after attaining this temperature decomposition began. The evolution of gases causes the pressure to rise rapidly. The rate was as high as 20 mm Hg/min.

Menzies [67], A. J. B. Robertson [66] and G. Edwards [69] have also carried out investigations on the vapour pressures of α– trinitrotoluene.

Edwards reported the following vapour pressures:

Temperature, °C	Pressure, cm Hg
60.1	5.43×10^{-5}
78.5	6.44×10^{-4}
80.2	7.16×10^{-4}
82.4	7.96×10^{-4}
99.5	4.07×10^{-3}
110.6	8.26×10^{-3}
131.1	3.48×10^{-2}
141.4	6.21×10^{-2}

Absorptivity. α– Trinitrotoluene is relatively strongly adsorbed on chromatographic columns and can be separated in this way from nitro derivatives of toluene with a lower number of nitro groups. Various columns have been suggested filled with basic adsorbents, but these were liable to produce a deep change in the trinitro compounds (Halfter [70], Ovenston [71]). A considerable improvement was reported by Kemula and his co-workers [72], using his chromate-polarographic method. Here the chromatographic column was filled with pulverized rubber swollen with n-heptane (immobile phase), the mobile phase being 0.2 M KI in a 50/50 methanol-water solution of the nitro compounds.

When the column was fed with a mixture of mono-, di- and tri-nitrotoluenes, *p*- nitrotoluene was eluted first, dinltrotoluene followed, and the last substance eluted was α– trinitrotoluene.

THERMOCHEMICAL PROPERTIES

Specific heat. C. A. Taylor and Rinkenbach [40] give the following values for α– trinitrotoluene at temperatures, ranging from 0°C to the melting point of the compound :

Temperature, °C	Specific heat, Cal/g °C
0	0.309
20	0.328
40	0.345
60	0.361
80	0.374

The *thermal conductivity*, λ, of α– trinitrotoluene is 0.00043 at 25° (Prentiss [73]).

Heat of crystallization and heat of evaporation. According to Tammann [74], the heat of crystallization of α– trinitrotoluene is 4.88 Cal/mole, and according to Edwards [69] is 5.6 Cal/mole. The heat of evaporation of α– trinitrotoluene, as found by Edwards [69], equals 22.7 Cal/mole. According to A. J. B. Robertson [66], it is 17.5 Cal/mole.

Heat of combustion and heat of formation. The heat of combustion of α– trinitrotoluene is 822.5 Cal/mole (Garner and Abernethy [3]). The value relates to constant volume and includes a correction that allows for the nitric acid formed in the calorimetric bomb.

From the measured heat of combustion, the heat of formation of α– trinitrotoluene has been calculated as +29.1 kcal/mole (assuming amorphous carbon), or +128.2 kcal/kg. Assuming the diamond form for carbon, Abemethy and Gamer [3] found a lower heat of formation, viz. +10.2 kcal/mole (Fig. 50. p. 261).

Other authors give the following values for the heat of formation of α– trinitrotoluene :

+ 16.0 kcal/mole (Kast [54])
+ 7.7 kcal/mole (Bichel [22])
+ 5.9 kcal/mole (Koehler [23])

For calculating the thermal effects of the processes in which α– trinitrotoluene takes part the values given by Gamer and Abernethy, or by Kast are generally used.

Heat of nitration. The heat of conversion of dinitrotoluene to trinitrotoluene, calculated from the heats of formation of the reactants and of the reaction products is:

+ 17.5 kcal/mole (starting product 1,2,4-dinitrotoluene) (Fig. 50)
+ 19.0 kcal/mole (starting product 1,2,6-dinitrotoluene)

Heat of explosion is discussed later (under explosive properties p. 318).

CHEMICAL PROPERTIES

Reactions with acids and alkalis

Like other aromatic nitro compounds, trinitrotoluene is resistant to the action of acids. Only concentrated nitric acid at a temperature over 110°C can oxidize it to 2,4,6-trinitrobenzoic acid, and at 200°C trinitrobenzene is formed, as a result of decarboxylation (p. 254).

However, trinitrotoluene reacts with alkalis, yielding organo-metallic products. The readiness of trinitrotoluene to react with alkalis has suggested the idea that it is an acid. This problem was studied by Farmer [75] in 1901. He applied a method, based on determining the partition coefficient K for trinitrotoluene between two liquid phases: water and benzene or water and ligroin phase, with addition of sodium hydroxide to the water phase.

While for picric acid a value $K = 0.164$ had been found by this method (Rothmund and Drucker [76]), for trinitrotoluene Farmer found $K = 2.0 \times 10^{-14}$, which means that trinitrotoluene is an acid 1013 times weaker than picric acid. In effect it has virtually no acidic properties.

Similarly Brand and his co-workers [77] inferred from the results of spectrophotometric studies that 2,4,6-trinitrotoluene, in a solution of 100% sulphuric acid, was not ionized, and could undergo partial ionization only in very concentrated oleum. These investigations are discussed more fully on p. 219.

On the other hand, attention should be drawn to the cryometric investigations of nitro compounds, already referred to (p. 218), which made Hantzsch express the view that the nitro group may confer a basic character to the compound. He gave only *p*- nitrotoluene as an example. Gillespie [78] has suggested that 2,4,6-trinitrotoluene in sulphuric acid solution also behaves as a base.

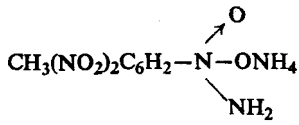
Wyatt and Brayford [79] have tried to explain the inconsistency of the spectrographic and cryometric results. On the basis of their cryometric measurements on solutions of 2,4,6-trinitrotoluene, 1,3,5-trinitrobenzene and picric acid in sulphuric acid in the presence of compounds interferring with the dissociation of the solvent, they finally concluded, on the basis of the spectrophotometric measurements, that polynitro compounds should be regarded as non-electrolytes.

Alkalis, when reacted with trinitrotoluene, very easily effect a considerable change in the substance, yielding red or brown coloured addition products containing metal. Inorganic acids separate from these products an organic substance, which is no longer trinitrotoluene. Numerous investigations carried out to elucidate the structure of this substance have given no definite answer as yet.

Several workers investigating trinitrotoluene many years ago took an interest in the nature of these substances (e.g. Wilbrand [34] in 1863; Hepp [35] in 1882).

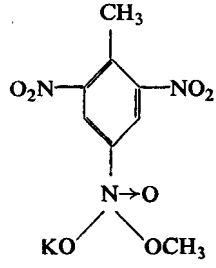
Korezynski [80] was one of the first who investigated the reaction quantitatively. In 1908 he introduced dry ammonia to various nitro compounds, including trinitrotoluene and trinitrobenzene. When the reaction was carried out at a low tem-

perature (-10°C), he found that one molecule of trinitrotoluene absorbs two of ammonia to form a complex to which the author ascribed the following formula:



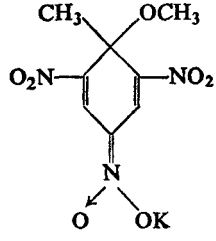
(cf. Faar, Bard and Wheland [160]).

Hantzsch and Kissel [81] by treating trinitrotoluene with potassium alcoholate (e.g. methylate) obtained an addition product to which they ascribed the structure given earlier by Angeli [82] for the product obtained from trinitrobenzene and CH_3OK (I).



I

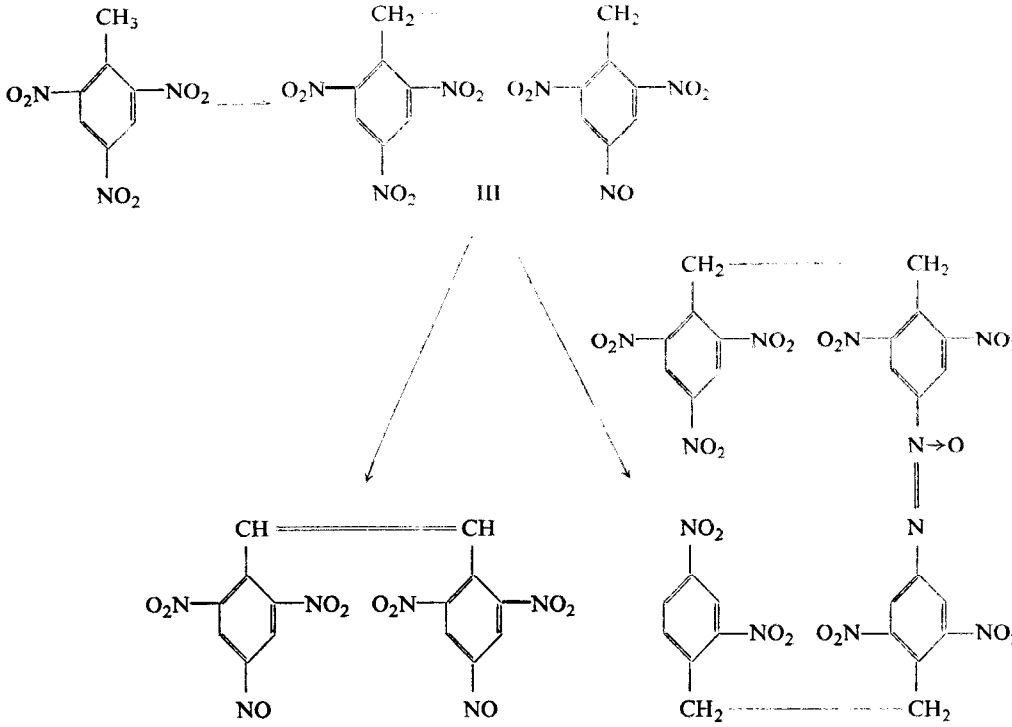
In accordance with Meisenheimer's work [83, 84] (p. 202), however, the structure should be presented by the formula II (using the more modem annotation).



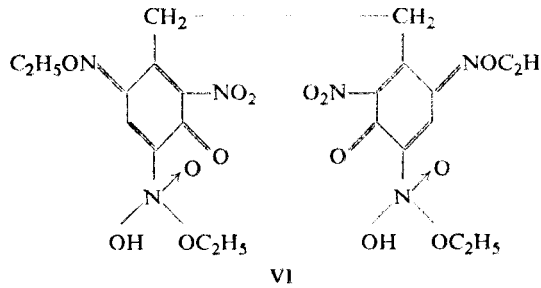
II

Further studies (Hantzsch and Picton [85]) showed, that inorganic acids, e.g. sulphuric, decompose these salts, with the evolution of nitrogen oxides. Products of a drastic transformation of trinitrotoluene are precipitated simultaneously, among them stilbene derivatives, products of oxidation of the methyl group.

Copisarow [86] tried to express the changes which trinitrotoluene undergoes under the action of alcoholates or alkali metal hydroxides by the following scheme, in which he postulated the formation of nitro-nitroso derivatives of dibenzyl (III), and stilbene (IV), followed by the formation of an azoxy compound (V), which might be transformed into more complex azoxy compounds:

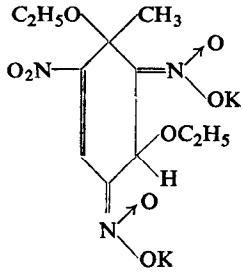


Giua and Reggiani [87] reacted sodium alcoholate with trinitrotoluene in acetone solution and obtained several addition products, containing various proportions of alcoholate (l-3 molecules of C_2H_5ONa for 1 molecule of trinitrotoluene). By treating the products with an inorganic acid, they obtained yellow, amorphous compounds, which they regarded as mixture of several substances, which were dibenzyl delivatives. e.g.:

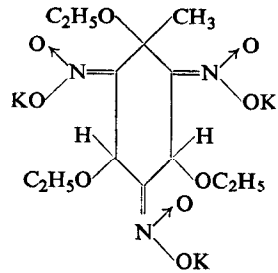


VI

Stefanovich [88], on the basis of Meisenheimer's formulae, ascribes the formulae VII and VIII to the addition products of α– trinitrotoluene with two or three molecules of potassium alcoholate respectively.



VII



VIII

He has stated that a maximum of three molecules of an alcoholate can be added to α– trinitrotoluene, the number being equal to the number of nitro groups.

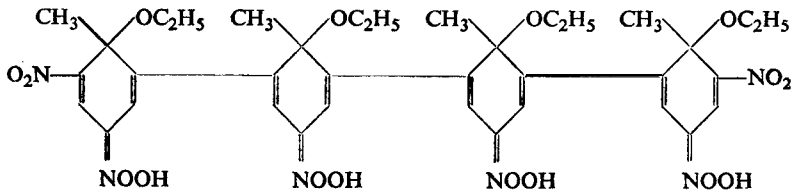
T. Urbanski and Pawlowski [89] investigated the salts formed on treating trimtrotoluene in acetone-alcohol solution with sodium alcoholate and also with an alcoholic solution of $Ba(OH)_2$. Various addition products were obtained, according to the proportion of the alcoholate or hydroxide, e.g.:

from $CH_3.C_6H_2(NO_2)_3 + C_2H_5OBa_{1/2}$ to $CH_3.C_6H_2(NO_2)_3 + 3C_2H_5OBa_{1/2}$

On acidification of these salts with sulphuric acid a pale yellow product was precipitated with simultaneous evolution of nitrogen oxides.

The pale yellow precipitate, “T acid”, dissolves in acetone, but it is insoluble in most organic solvents, thus differing from TNT. It has an acid character and is able to form salts.

T. Urbanski [90] assumes that it has the structure of the diphenyl-diphenylene compound (IX) :



IX

The explosive properties of the compound TX differ considerably from those Of trinitrotoluene. Its explosive power is much lower than that of trinitrotoluene, which may be explained by the smaller number of the nitro groups present. Both “T acid” itself, and also its salts, are much more sensitive to mechanical and thermal stimuli than trinitrotoluene.

T. Urbaliski and Pawlowski [89] obtained the following characteristic values:

"T acid" ignites, when heated to	210°C after 4 see
	225°C ,, 0.5 ,,
Sodium salt of "T acid" at	185°C ,, 4 ,,
	200°C ,, 0.5 ,,
Copper salt of "T acid" at	210°C ,, 4 ,,
	225°C ,, 0.8 ,,
Ferric salt of "T acid" at	220°C ,, 4.5 ,,
	235°C ,, 0.6 ,,
Zinc salt of "T acid" at	230°C ,, 3.5 ,,
	245°C ,, 0.8 ,,

"T acid", when contacted with a flame, ignites instantaneously like dry nitrocellulose. Salts of "T acid" ignite just as readily. Its sensitivity to impact is also very high, being of the same order as tetryl.

According to Bowden [91], the initiation temperature of the product of prolonged treatment of TNT with moist ammonia (for 66 hr) is merely 67°C. This observation has not been confirmed by other authors, who found the initiation temperature of the product to be about 250°C, i.e. of the same order as that of TNT (290°C) within the limits of experimental error. Even if not all authors agree with Bowden's low figure for the temperature of initiation of the products obtained by reacting trinitrotoluene with alkalis, it has been stated repeatedly that these products are much more sensitive to heat, impact and friction than trinitrotoluene itself. Their high sensitiveness is of greatest practical importance, and is a warning that great care should be taken to avoid bringing TNT into contact with alkalis, especially in the presence of organic solvents such as alcohol, acetone etc.

There is evidence that the reaction product of trinitrotoluene with potassium alcoholate, which explodes when heated to 130-150°C, may even ignite spontaneously at room temperature.

According to Dupre [92], the ignition temperature of trinitrotoluene is considerably lowered by the addition of various substances, e.g. sulphur, phosphorus, aniline black. When potassium hydroxide is added at 160°C, trinitrotoluene ignites or explodes immediately. A mixture of powdered trinitrotoluene and powdered potassium hydroxide ignites when heated to 80°C. A mixture with sodium hydroxide behaves similarly although the reaction is less vigorous, On rapid heating, ignition occurs at a temperature of 80°C but on slow heating the mixture does not explode; even at 200°C - only gradual decomposition takes place.

When a piece of potassium hydroxide is put into molten trinitrotoluene at 100°C, it becomes coated with a film that prevents it from reacting further. But on addition of a drop of alcohol, which dissolves both trinitrotoluene and potassium hydroxide, the mixture ignites at once.

Reaction with inorganic substances

A. J. B. Robertson [66] investigated the influence of various substances on the rate of thermal decomposition of trinitrotoluene. He measured the diminution

of the induction period (i.e. the period of time elapsing between the application of heat to the sample and the moment of explosion), brought about by the addition of foreign matter to trinitrotoluene (Table 68).

TABLE 68

INFLUENCE OF ADMIXTURES ON THE INDUCTION PERIOD OF THERMAL DECOMPOSITION OF α– TRINITROTOLUENE

Admixture	Temperature °C	Diminution of the induction period, t, by sec
1.9% of Fe_2O_3	297	3.9
11% of ferro-a-nitroso-*p*- naphthol complex	276	45
9% of diphenylamine	287	14

The induction period for pure trinitrotoluene at 275°C is 12 min and at 328°C-50 sec.

As T. Urbanski and Pillich [93] found, the addition of sulphur to TNT causes the initiation temperature to fall. This can be seen from the following data:

Sulphur content, %	Initiation temperature, °C
Pure TNT	333
5	304
10	294
20	284
30	275

The explosion caused by heating TNT to which 5-10% of sulphur has been added is more violent than the explosion of pure TNT.

Investigations on the influence of metals on TNT are of special importance. Extensive studies on the effect of lead, aluminium and iron on TNT in the presence of nitric acid were carried out by Kovache and Thibon [94] as early as in 1918. These investigators found, that when heating TNT with chips of lead, aluminium or iron in the presence of nitric acid diluted with water to a concentration of about 13% of HNO_3, a product was formed which contained a considerable proportion of the metal, and which was insoluble in toluene, inflammable and sensitive to friction and impact. The products of the reactions of TNT with lead and iron were particularly sensitive. They also could be ignited when heated with nitric acid or with mixtures of nitric and sulphuric acids.

The constitution of these products has not been determined. It is possible that they arc mixtures of complex compounds of various composition. The lead content in the product obtained in the reaction with lead provides evidence of variable com-

position. The lead content varies from 23.5 to 64.5% Pb, depending on the mode of their preparation.

On reacting TNT with metals in the presence of mixtures of nitric and sulphuric acids diluted with water similar products were obtained, although the presence of sulphuric acid inhibited their formation to some extent. These products can be formed in production while TNT is being washed free of acid by water, for when most of the sulphuric acid has been removed, the remaining nitric acid is strongly absorbed by molten TNT.

According to the Kovache and Thibon, these metal compounds may be formed in several lead or iron parts of the plant and are a potential cause of accidents.

Kovache and Thibon also found that similar inflammable metal products were formed by lower nitrated toluene derivatives, e.g. *p*- nitrotoluene and 2,4-dinitrotoluene, and also by trinitrobenzene. Nitrobenzene and trinitroxylene did not react in this way.

It seems certain that the products discussed have fairly complex structures, being the result of a partial reduction of a nitro group (or groups) by the metal in an acid medium, followed by oxidation by nitric acid. The oxidation leads to ill-defined inflammable products of high molecular weight.

Effect of heat

Trinitrotoluene is very resistant to heat. Extensive investigations of this property of TNT have been carried out by Kast [54] and Verola [68], both of whom obtained consistent results.

According to Verola, heating TNT at 130°C for 100 hr does not bring about any decomposition. Kast, when heating trinitrotoluene at 150°C for 4 hr, found no gases evolved from its decomposition. According to Verola, a distinct evolution of gaseous decomposition products starts at 160°C.

Kast established that at a temperature of 240°C, trinitrotoluene ignites in 0.5 hr. At 270°C marked exothermic decomposition takes place. Temperatures from 295-330°C are the true ignition temperatures of TNT (Verola found 281-286°C). According to Micewicz and Majkowski [95], the ignition temperature of TNT is 312-318°C.

Verola has also examined the effect of prolonged heating on the melting point of TNT. Heating at 145-150°C gave the following results:

	m. p., °C
Before the experiment	80.75
After 18 hr heating	80.66
After 42 „ „	80.55
After 80 „ „	80.25
After 127 „ „	80.20
After 158 „ „	80.13
After 177 „ „	79.90

In another set of experiments Verola obtained:

	m.p. °C
After heating for nearly 290 min at 180°C	78
After heating for nearly 180 min at 201°C	17
After heating for nearly 45 min at 217.5°C	59

TNT is difficult to ignite. When heated directly in a flame it melts, and ignites only when brought to a high temperature (about 300°C). For this reason the view has been accepted that TNT is safe to handle at high temperatures and in the presence of a flame.

However, the fact should be taken into account that molten TNT is more sensitive to impact than in the crystalline state (p. 320, Table 75, Fig. 74). Moreover, if large quantities of TNT ignite, combustion might proceed very vigorously, and even cause detonation.

Experiments carried out after the accident described on p. 393 have shown that a lighted cigarette, thrown onto a sack containing about 50 kg of TNT, is able to cause the TNT to detonate.

Effect of light

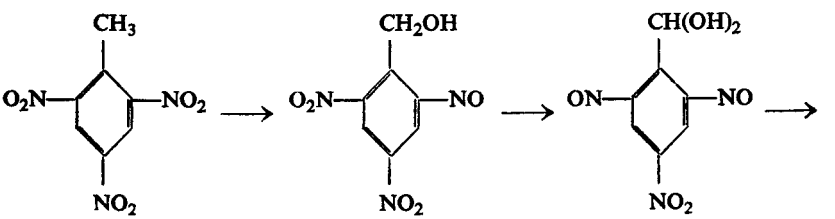
It has long been known that trinitrotoluene undergoes far-reaching changes under the influence of sunlight. Dark coloured products are formed, the structure of which is not yet fully understood.

In 1907 Kast [57] found that the melting point of trinitrotoluene fell from 80.0°C to 795°C after irradiation for a fortnight.

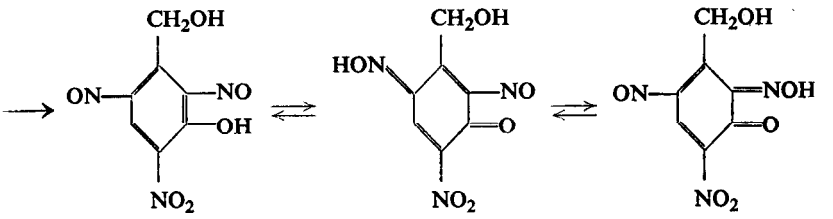
Molinari and Giua's investigations [96] showed that the melting point of trinitrotoluene which has been exposed to sunlight for 3 months in the open fell from 80°C to 74°C. When, however, trinitrotoluene was irradiated in absence of air in vacuum, hardly any changes in colour and melting point were observed.

According to Oddo [97] and Lodati [98], under the influence of radiation trinitrotoluene partly loses nitrogen and is transformed into a compound of acidic character.

Schultz and Ganguly [99] suggest that trinitrotoluene undergoes a number of isomerization processes, consisting in transferring the oxygen of a nitro group to the methyl group (as in Ciamician and Silber's reaction). The nitro compound XIII reacts like quinone oxide (XIVa and XIVb):



XI XII



XIII XlVa XIVb

The authors isolated the intermediate product XI but the products XII and XIII are hypothetical.

Naoum [100] found that trinitrotoluene, when exposed to light, yields a product of the formula $C_{14}H_8O_{10}N_5$, insoluble in benzene or water, and exceptionally sensitive to impact. In addition, a water-soluble red dye is formed.

Krauz and Turek's suggestion [101] that on exposure to sunlight mainly picric and trinitrobenzoic acids are formed has not been confirmed by other authors (Wichert and Donat [102]).

The fact that trinitrotoluene undergoes marked changes when exposed to sunlight indicates the necessity of shielding it against radiation. All the windows in TNT factory buildings should be protected against the sunlight (e.g. painted blue).

Reaction with sodium sulphite

α– Trinitrotoluene reacts only very slowly with aqueous solutions of sodium sulphite, thus differring from its unsymmetrical isomers which can react very rapidly (p. 332). The trend of the reaction of α– trinitrotoluene may also be different. α– Trinitrotoluene reacts with dilute (5%) solutions of sodium sulphite at room temperature to yield red coloured addition products. According to Muraour [103]. at room temperature

a 3% solution of sodium sulphite dissolves 0.3% α– trinitrotoluene
a 6% ., ,, ,, ,. 0.6%
a 12% ,, ,, ,, ,, 2.3% .,

α– Trinitrotoluene can be recovered from the solutions by acidifying it or simply by dilution with water.

At higher temperatures, however, the α– trinitrotoluene undergoes a more drastic transformation. This is the result of both the action of Na_2SO_3 and of the high pH of the solutions: one NO_2 group is substituted by an SO_3Na group. Thus the reaction proceeds in essentially the same way as in the case of the unsymmetrical isomers.

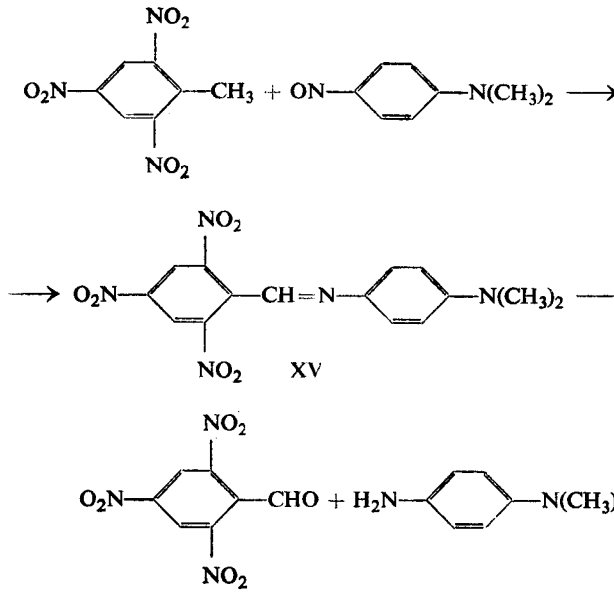
$$CH_3C_6H_2(NO_2)_3 + Na_2SO_3 \rightarrow CH_3C_6H_2(NO_2)_2SO_3Na + NaNO_2$$

For more details see also pp. 332-335.

Other reactions

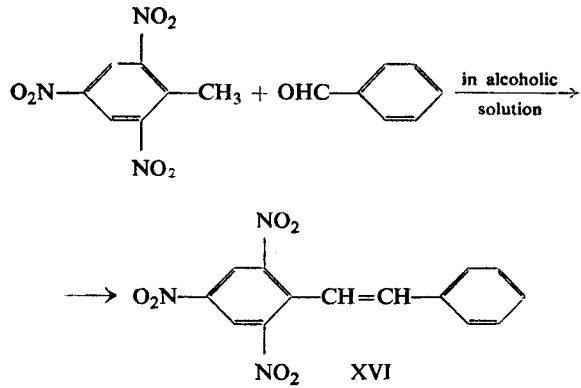
The methyl group in trinitrotoluene becomes strongly activated by the nitro groups present. This could be ascribed to the hyperconjugation of toluene (p. 200)

strongly reinforced by the induction effect of three nitro groups. This is why trinitrotoluene readily reacts with *p*- nitrosodimethylaniline in the presence of hydroxides to form an anil (XV), which then hydrolyses to trinitrobenzaldehyde:



(13)

Trinitrotoluene reacts in a similar way with benzaldehyde in an alkaline medium to form a stilbene derivative:



(14)

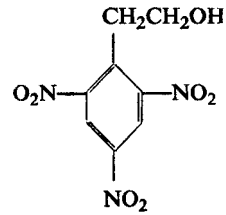
The reaction is strongly exothermic. For example, a mixture of trinitrotoluene and benzaldehyde, in the absence of a solvent, reacts when a few drops of piperidine are added. The reaction is so violent that the mixture may ignite. The methyl group of trinitrotoluene reacts with other aldehydes in a similar way. For this reason trinitrotoluene should be protected against the action of aldehydes, especially in alkaline media. Aldehydes may be formed under the influence of acids on wood. Hence, wooden vats which were formerly used for washing TNT are hardly used. now.

According to Heinke [104], trinitrotoluene reacts with diazomethane, three molecules of the latter losing their nitrogen atoms and combining with a molecule of trinitrotoluene as methylene groups, the fourth molecule of diazomethane being directly attached to the same molecule of trinitrotoluene:

$$C_6H_3N_3O_6 + 4CH_2N_2 \rightarrow C_{10}H_{11}N_5O_6 + 3N_2 \quad (15)$$

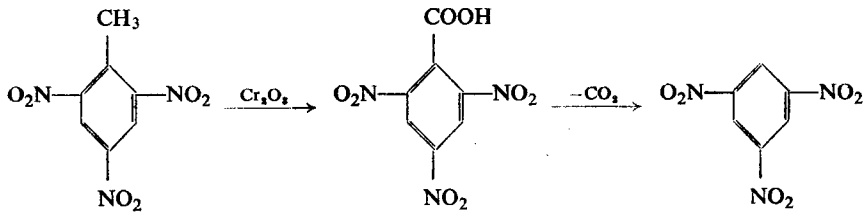
The constitution of the product has been determined by de Boer [161].

The reactivity of the methyl group in trinitrotoluene is also evident in the reaction with formaldehyde, a molecule of the latter being attached to form a trinitro derivative of phenylethyl alcohol (XVII) [162]:



XVII

The methyl group is readily oxidizable, giving rise to trinitrobenzoic acid which, because of the accumulation of nitro groups, is unstable and in turn loses its CO_2 to form trinitrobenzene:



Addition products

Trinitrotoluene, like other highly nitrated aromatic hydrocarbons, easily forms addition products with polycyclic hydrocarbons and amines. The addition products formed by α– trinitrotoluene have been extensively studied by Hepp [35] and Kremann [104a,104b]. Some of the products are listed below (Table 69).

α– Trinitrotoluene also forms addition compounds (1 : 1) with α– nitronaphthalene m. p. 64.7 (melts with simultaneous dissociation) (Wogrinz and Vári [105]; Taylor and Rinkenbach [40]; Frolova [106]).

The β– and γ– isomers of trinitrotoluene also form molecular compounds (1 : 1) with naphthalene, acenaphthene, fluorene, phenanthrene and anthracene (Jefremov and Bogush [107]; Jefremov and Frolova [107a]).

According to T. Urbaliski [log], α– trinitrotoluene forms with erythritol tetranitrate an unstable addition compound, (4 : l), melting at about 65°C.

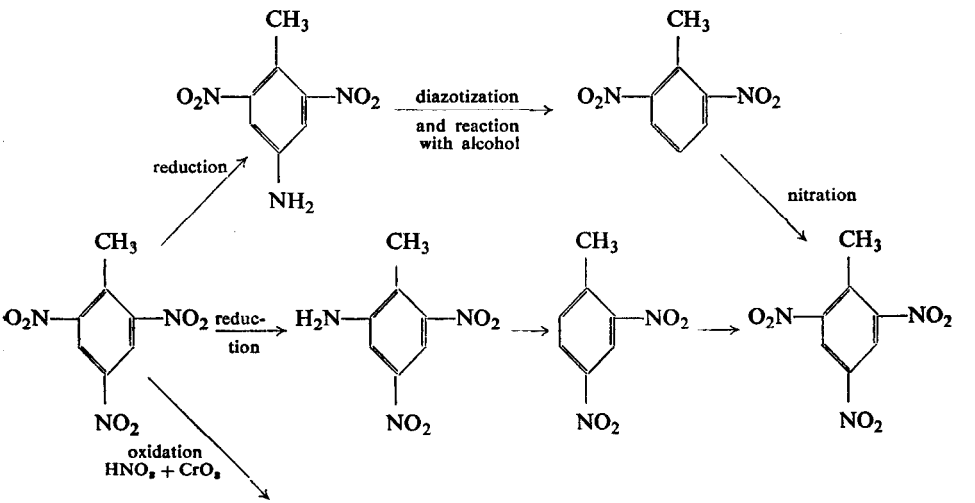
The composition of various eutectics of α– trinitrotoluene were given on p. 295.

TABLE 69

Hydrocarbon or amine, etc.	Molecular proportion α– trinitrotoluene/second component	Melting point °C	Form
anthracene	1:1	102.5	brown-yellow needles
acenaphthene	1:1	112.0	
phenanthrene	1:1	87.5	
fluorene	1:1	85.0	
naphthalene	1:1	96.5	straw yellow needles
aniline	1:1	83-84	red needles
dimethylaniline	1:1	-	violet needles
diphenylamine	2:3	31.0	red needles
carbazoie	1:1	~ 140.0	yellow needles
α– naphthylamine	1:1	141.5	dark red needles
&naphthylamine	1:1	113.5	light red needles
benzyl-/?-naphthyhunine	1:1	106.5	purple needles
dibenzyl-&naphthylamine	1:1	108.0	brick red needles
o-toluidine	1:1	53-55	light red needles
m-toluidine	1:1	62-63	light red needles
benzaldehyde phenyl-hydrazone	2:1	84	dark red needles

ELUCIDATION OF THE CONSTITUTION OF α– TRINITROTOLUENE

The constitution of α– trinitrotoluene has been established on the basis of the following reactions [36]



see eqn. (16) p. 310.

KINETICS OF THE NITRATION OF DINITROTOLUENE TO TRINITROTOLUENE

From the results of their studies on the kinetics of the nitration of 2,4-dinitrotoluene to 2,4,6-trinitrotoluene Bennett and his co-workers [109, 110] inferred that the reaction is of the third order, represented as follows:

$$DNT + NO_2^+ + HSO_4^- \rightarrow TNT + H_2SO_4 \quad (17)$$

$$DNT + NO_2^+ + H_2SO_4 \rightarrow TNT + H_2SO_4 \quad (18)$$

In the presence of oleum the reaction

$$DNT + NO_2^+ + HS_2O_7^- \rightarrow TNT + H_2S_2O_7 \quad (19)$$

may also take place.

The rate of the nitration reaction in the presence of sulphuric acid can be re presented by :

$$\frac{d[TNT]}{dt} = k[DNT][NO_2^+][HSO_4^-] + k'[DNT][NO_2^+][H_2SO_4] \quad (20)$$

The constants ***k*** and ***k'*** are independent of the medium and of the concentration of sulphuric acid. If Q denotes the proportion of nitric acid dissociated into NO_2^+ ions, then :

$$[NO_2^+] = Q\,[HNO_3] \quad (21)$$

From this the following equation for the rate of nitration can be derived:

$$\frac{d[TNT]}{dt} = \{k[HSO4-] + k'[H_2SO_4]\}[DNT][HNO_3]Q \quad (22)$$

At a constant concentration of sulphuric acid the nitration rate can be represented by a second order reaction equation:

$$\frac{d[TNT]}{dt} = k_2[HNO_3][DNT] \quad (23)$$

where k_2 is the rate constant of a second order reaction.

From equation (22) Bennett and his co-workers derived the following general equation valid when oleum is used:

$$\frac{d[TNT]}{dt} = k\,[HSO_4^-] + k'[H_2SO_4] + k''[HS_2O_7^-][DNT][HNO_3]Q \quad (24)$$

Values of ***k, k'*** and ***k"*** for concentrations of sulphuric acid ranging from 87.4% H_2SO_4 to oleum containing 29.1% SO_3, at temperatures from 60°C to 120°C, have been determined experimentally.

The experiments are in agreement with the equations derived. In particular, the equations show that an increase in the reaction rate due to decreasing the con-

centration of sulphuric acid from 100 to 92% may be explained by the fact that the concentration of HSO_4^- ions increases considerably, whereas the concentration of NO_2^+ ion decreases only slightly. Decreasing the concentration of sulphuric acid below 92% H_2SO_4 causes the NO_2^+ concentration to fall more rapidly than the HSO_4^- concentration increases, thus decreasing the reaction rate.

To check their theory, Bennett and his co-workers added $KHSO_4$ to the nitrating mixture. As they expected, at concentrations of acid over 92% the reaction rate increased. According to the theory, this was the result of increasing the concentration of HSO_4^- ions. However, at concentrations below 92% of H_2SO_4, adding $KHSO_4$ caused the reaction rate to fall, as increasing the concentration of the HSO_4^- ions resulted in a decrease in the concentration of NO_2^+ ions (Fig. 65).

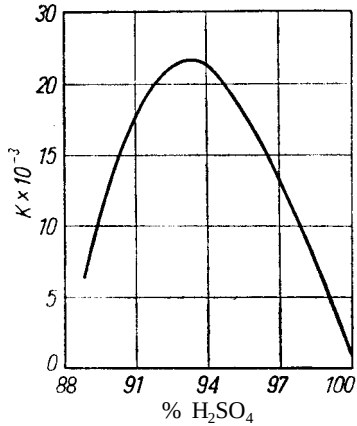


FIG. 65. Influence of the concentration of sulphuric acid on the rate of nitration of DNT in a heterogeneous medium (nitrating mixtures with a low content of HNO_3, Bennett et al. [110])

As pointed out earlier (p. 36) the concentration of the proton acceptor (HSO_4^- in our instance) is not the only factor determining the rate of nitration.

If the concentration of HSO_4^- appears to have a considerable influence on the rate of reaction this may be due to the fact that in concentrated nitrating mixtures (over 92% H_2SO_4) a high concentration of HSO_4^- is accompanied by 8 high concentration of NO_2^+.

However, the equations of Bennett are useful for calculating the rate of nitration of dinitrotoluene to trinitrotoluene.

Orlova [110a] repeated the experiments of Bennett et al., studying the kinetics of nitration of dinitrotoluene in nitrating mixtures rich in nitric acid that dissolve dinitrotoluene, i.e. in homogeneous conditions. For 0.7 mole of dinitrotoluene, 3.8 mole of HNO_3 in 12 mole of H_2SO_4 were used. The concentration of sulphuric acid was changed from 87 to 100% H_2SO_4. The temperature was 90°C. Contrary to the results of Bennett, Orlova did not find any maximum of the rate of nitration (Fig. 66) which she attributes to the homogeneity of the reaction medium.

Orlova [2a] also studied the change in rate of nitration of dinitrotoluene under the action of stirring. The reaction was carried out with a nitrating mixture containing 16% HNO_3, 81% H_2SO_4; ratio nitrating mixture/dinitrotoluene = 1.5, temperature 90°C, time 40 min. Orlova found that above a certain rate of stirring no improvement of the yield was obtained (Fig. 67).

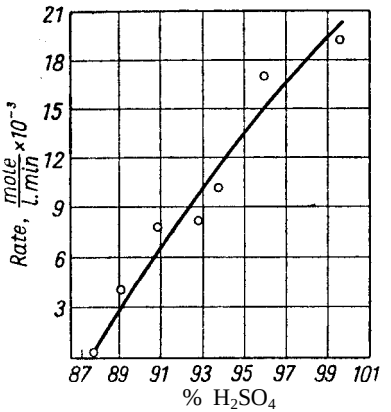


FIG. 66. Influence of the concentration of sulphuric acid on the rate of nitration in homogeneous conditions (nitrating mixtures with a high content of HNO_3, Orlova [2a]).

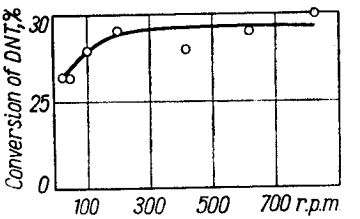


FIG. 67. Influence of the rate of stirring on the rate of nitration of DNT (Orlova [2a]).

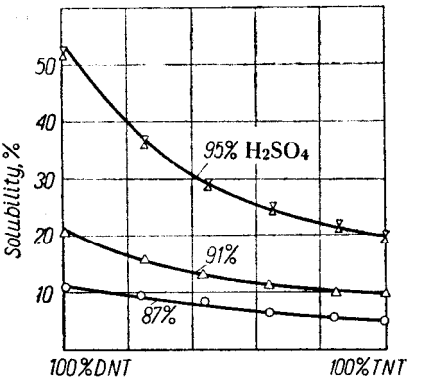


FIG. 68. Solubility of DNT and its molten mixtures with TNT in sulphuric acid of various concentrations (Orlova [2a]).

Another important factor governing the nitration of dinitrotoluene is the distribution of dinitrotoluene between the two phases: the organic phase consisting of trinitrotoluene (and dinitrotoluene) and the acid phase. The solubility of 2,4-dinitrotoluene in concentrated sulphuric acid is considerably diminished when 20-30% of trinitrotoluene is dissolved in the dinitrotoluene. Further addition of trinitrotoluene reduces the solubility to a lesser extent. This can be seen from Table 70 and Fig. 68.

The overall low solubility of nitro compounds in the acids causes the distribution coefficient of dinitrotoluene being very low (0.3-0.4). The distribution coefficient of dinitrotoluene when a 50 : 50 mixture of 2,4-dinitrotoluene and α– trinitrotoluene was

TABLE 70
SOLUBILITY OF 2,4-DINITROTOLUENE AND α– TRINITROTOLUENE MIXTURES IN SULPHURIC ACID

Content of 2,4-dinitrotoluene in mixtures with α– trinitrotoluene	Solubility of the mixtures (in %) in sulphuric acid of different concentration		
%	87%	91%	95%
100	10.7	21.5	54.0
76	9.0	16.0	36.0
55	8.7	14.7	30.4
35	7.7	12.0	25.7
16.6	6.9	11.5	22.5
0	6.1	10.6	19.7

TABLE 71
COEFFICIENT OF DISTRIBUTION OF DINITROTOLUENE BETWEEN THE MINERAL AND ORGANIC LAYERS

Temperature, °C	70	80	85	90
Dissolved % of the mixture	16.8	17.9	19.3	19.0
composed of: DNT	13.8	12.9	12.1	8.9
TNT	3.0	5.0	7.2	10.1
Coefficient of distribution $R = \frac{\%\ \text{DNT in mineral layer}}{\%\ \text{DNT in organic layer}}$	0.32	0.29	0.26	0.18

treated with 90% sulphuric acid at different temperatures is given in Table 71 and Fig. 69. Figure 70 shows the influence of the concentration of sulphuric acid at 90°C.

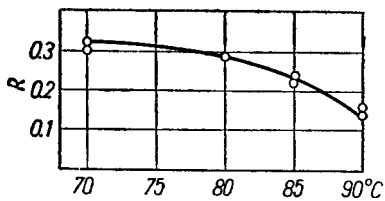


FIG. 69. Influence of the temperatur : on the distribution coefficient ***R*** of, DNT between the mineral and organi layers (Orlova [2a]).

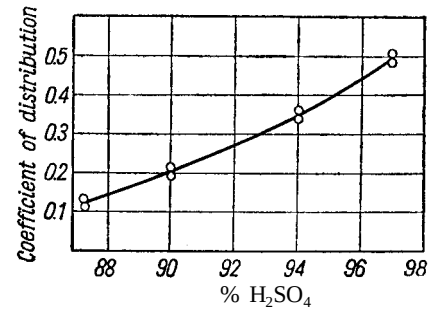


FIG. 70. Influence of the concentration of sulphuric acid on the distribution coefficient ***R*** of DNT between the mineral and organic layer (Orlova [2a]).

Another important feature in the nitration of dinitrotoluene is the coefficient of distribution of nitric acid between the mineral and organic layers. The data for sulphuric acid of 93% H_2SO_4 at 90°C are given in Table 72.

TABLE 72

INFLUENCE OF CONCENTRATION OF HNO_3 IN THE NITRATING MIXTURE ON THE RATE OF NITRATION OF DNT AND THE COEFFICIENT OF DISTRIBUTION OF HNO_3 BETWEEN THE MINERAL AND ORGANIC LAYERS

Concentration (in %) of HNO_3 in nitrating mixture	6.1	9.3	17.7	22.7	35.6	38.8	41.5
Yield of TNT (in mole/l.)							
in homogeneous system	0.420	0.455	0.510	0.535	0.375	-	-
in heterogeneous system	0.326	0.394	0.450	0.435	0.550	0.492	0.357
Coefficient of distribution of HNO_3							
% HNO_3 in mineral layer / % HNO_3 in organic layer	1.24	1.20	**1.62**	0.84	0.99	0.91	1.05

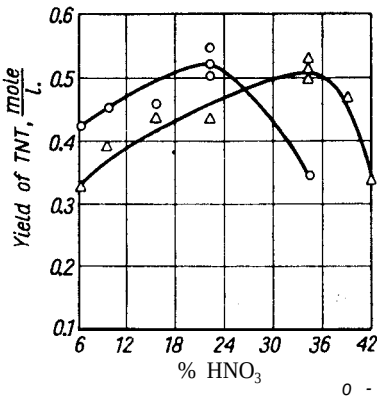


FIG. 71. Influence of the content of HNO_3 in nitrating mixtures on the rate of nitration of DNT to TNT (Orlova [2a]).

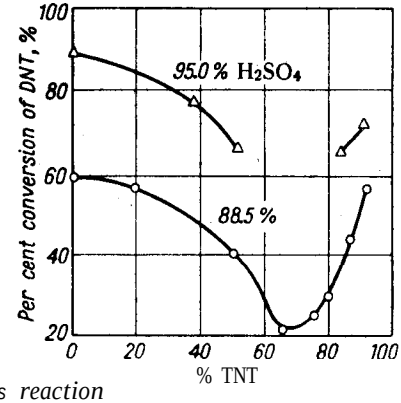


FIG. 72. Change of the rate of nitration of DNT in the presence of TNT (Orlova [2a]).

In both homogeneous and heterogeneous systems the rate of reaction increases and then falls with increasing concentration of nitric acid (Fig. 71). In heterogeneous systems the maximum corresponds to higher concentrations of HNO_3. The difference can be explained in terms of coefficient of distribution. Hence the concentration of HNO_3 in the mineral phase of the heterogeneous system reaches the value corres-

ponding to the maximum rate of nitration when the total concentration is higher than in the homogeneous system.

This results from the rule already observed that nitration of aromatic compounds occurs mainly in the mineral acid phase.

When a large excess of nitric acid is used there is very little difference between the rate of nitration in heterogeneous and homogeneous systems. This is due to the larger excess of nitric acid present in the mineral acid phase.

Orlova has also investigated the influence on the rate of nitration of the presence of trinitrotoluene in dinitrotoluene. Table 73 gives the corresponding figures obtained in sulphuric acid of various concentrations at 100°C. The nitrating mixtures contained 10% HNO_3:

TABLE 73

YIELD OF TRINITROTOLUENE WHEN MIXTURES OF DINITROTOLUENE AND TRINITROTOLUENE ARE NITRATED

Content of TNT in the original mixture of DNT and TNT	% of dinitrotoluene nitrated within 30 min-- at concentration of sulphuric acid (in % H_2SO_4)					
%	87	91	95	98	101	104
0	7.8	21.0	22.0	-	–	-
24	7.1	19.5	22.0	-	-	-
45	2.0	18.2	22.0	-	-	-
64	0	17.5	27.5	-	-	-
84	0	26.0	48.3	74.0	75.0	78.4
92	-	-	47.0	81.1	82.7	83.9

Figure 72 shows the influence of trinitrotoluene on the rate of nitration of dinitrotoluene in heterogeneous systems at 90°C. It is interesting to note that the addition of 66-70% of trinitrotoluene to dinitrotoluene more than halves the rate of the nitration, Further increase in the content of trinitrotoluene promotes nitration of dinitrotoluene. When the content of trinitro compound reaches 91% the yield of trinitration is almost the same as that of the pure dinitrotoluene.

On the basis of her own experiments and those reported in the literature Orlova [2a] came to the conclusion that the mechanism of nitration of toluene to TNT in heterogeneous conditions can be depicted in the following terms.

Nitration of toluene to mononitrotoluene and of the latter to dinitrotoluene in heterogeneous conditions should be considered mainly a “surface” reaction. This is deduced from the fact that the rate of the reaction depends on the intensity of stirring. The reaction of nitration of dinitrotoluene to trinitrotoluene in heterogeneous system is not limited to the surface dividing the two phases. This is proved by the fact that the rate of nitration depends very little on the rate of stirring. The reactants - dinitrotoluene and nitric acid - are distributed between two phases according to their coefficients of distribution and to the ratio between

the volumes of the two phases. The reaction occurs in both phases but the rate in the mineral acid phase is much higher than in the organic oil phase. In the latter it is relatively high only when the factor " Φ " is high.

This is because the organic oil phase contains only HNO_3 with practically no H_2SO_4. The rate of nitration of dinitrotoluene depends therefore largely on the solubility of dinitrotoluene in the acid layer.

To some extent the organic phase has a negative action on nitration. It is a good solvent of HNO_3 and considerably reduces the concentration of HNO_3 in the acid phase.

The secondary reaction of oxidation occurs in both the organic and mineral layers. It is likely that oxidation occurs strongly in the organic layer because of the presence of HNO_3 free from H_2SO_4.

The negative influence of the organic layer also consists in reducing the concentration of dinitrotoluene in the mineral acid phase. This occurs when the organic phase is composed mainly of molten trinitrotoluene. The distribution coefficient of dinitrotoluene between the two phases shifts the dinitrotoluene towards the organic layer. This particular negative action of the trinitrotoluene layer is less pronounced by the end of the nitration when very little dinitrotoluene is left unnitrated. To favour the reaction it is necessary to raise the temperature. Therefore the most favourable condition of heterogeneous nitration exists at the beginning of the reaction when the organic layer is composed only of dinitrotoluene. Therefore at this stage of the reaction it is possible to use less concentrated nitrating mixtures and a lower nitration temperature.

EXPLOSIVE PROPERTIES OF TNT

Decomposition of TNT during detonation, dependent on a number of factors. may be represented (Kast [57]) by the following equation:

$$16C_7H_5(NO_2)_3 = 20CO_2 + 47CO + CH_4 + H_2O + 2C_2H_2 + 2HCN + 14.5\ H_2 + 21.5\ N_2 + \\ + 3NH_4HCO + 29C$$

The heat of explosion of TNT is 950 kcal/kg, the volume of gases V_0 = 690 l/kg, the temperature t = 2820°C.

Schmidt gave [111] a number of the equations for TNT decomposition; calculated on 1000 g (4.4 moles) of trinitrotoluene. Here are two of them, for the extreme density of loadings d = 1.0 and 1.59 g/cm^3

(1) for A = 1.0 g/cm^3

$$4.4C_7H_5(NO_2)_3 = 2.84CO_2 + 17.0CO + 3.77H_2O + 2.49H_2 + 0.1C_mH_n + 0.1CH_4 + \\ + 2.85NH_3 + 0.47HCN + 0.2C_2N_2 + 4.75N_2 + 10C$$

The heat of explosion = 910 kcal/kg, the volume of gases V_0 = 773 l./kg, t = 3080°C.

(2) for d = 1.59 g/cm^3

$$4.4C_7H_5(NO_2)_3 = 5.47CO_2 + 9.39CO + 6.09H_2O + 1.63H_2 + 0.03C_mH_n + 0.42CH_4 + \\ + 1.5NH_3 + 0.32HCN + 0.3C_2N_2 + 5.39N_2 + 14.6C$$

The heat of explosion = 1085 kcal/kg, the volume of gases V_0 = 685 l./kg. I = 3630°C.

According to R. Robertson and Garner [112], the heat of explosion of TNT is 925 kcal/kg, and the volume of gases is 711 l./kg.

The sensitiveness of TNT to impact is very small, but because of the lack of a standard testing method, the data, reported by various authors, range within wide limits. Taking 100 for the sensitiveness of picric acid, values varying from 115 to 275 are quoted for TNT.

With increasing temperature the sensitiveness of TNT to impact increases like that of other explosives. This can be seen from Table 74, given by Rinkenbach [113].

TABLE 74
EFFECT OF TEMPERATURE ON THE SENSITIVENESS OF TNT TO IMPACT

Temperature °C	State of TNT	Height from which 2 kg weight must fall to cause explosion, cm
-40	solid	43
20	solid	36
80	liquid	18
90	liquid	7.5
105-110	liquid	5

Robertson [113a], however, reported that the sensitiveness of picric acid at 80°C is only 25% greater than that at 15°C. This may well be extended to other trinitro compounds, so it would be expected that the increase in sensitiveness of TNT with increasing temperature is less significant than that given by Rinkenbach.

T. Urbanski and Sikorska [141] recently determined sensitiveness to impact by means of the "piston apparatus" [115] (Fig. 73) as it gives uniform results at elevated temperature. The percentage of explosions were determined by striking the samples with a falling weight of 10 kg from heights of 25, 30 and 50 cm. The recoils were 4.5, 5 and 11 cm, and the calculated impact energies for a surface were 2.7, 3.1 and 5.0 kgm/cm^2 respectively. The experiments were repeated 100 times at each height.

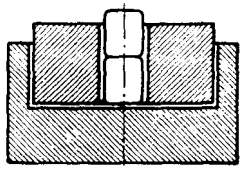


FIG 73. "Piston apparatus" of Kholevo-Andreyev [115] for determination of sensitiveness of explosives to impact.

The results are tabulated (Table 75) and presented in diagrammatic form (Fig. 74). There is a characteristic increase of the slope of the line of sensitiveness above the melting point of TNT. It is evident that the sensitiveness of molten TNT between 81°C and 100°C is well below that of tetryl at room temperature.

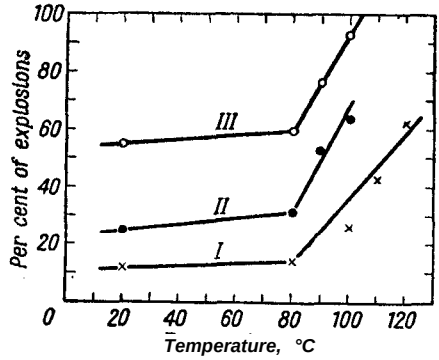


FIG. 74. Sensitiveness Of TNT to impact at various temperatures (T. Urbanski and Sikorska [114]).

TABLE 15

Substance	Temperature °C	Per cent of explosions at the height of		
		25 cm curve *I*	30cm curve *II*	50cm curve *III*
TNT	18	-	24	54
	20	**11**	-	-
	80	13	-	-
	81		31	59
	90	-	48	75
	100	25	63	89
	110	43	-	-
	120	62	-	-
Picric acid	18	-	50	75
Tetryl	18	48	81	94

The sensitiveness of TNT at 90°C is of the order of that of picric acid at room temperature.

In any case the handling of liquid TNT requires more safety measures than solid TNT, though the fact that detonation in molten TNT proceeds only with great difficulty reduces the danger. TNT becomes more sensitive when such solid substances as for example ammonium nitrate, are added to it (Vol. IV). Addition of sulphur also increases the sensitiveness to impact (T. Urbanski and Pillich [93]).

The sensitiveness of TNT to friction is also very low, but becomes higher when TNT is in the molten state.

TNT gives a lead block test figure of 260-310 cm^3, according to various authors, which is 94-98% of that given by picric acid. In a mortar it gives a value 90% of that for picric acid and its sand test value is 95% of that for picric acid.

The rate of detonation of TNT, as reported by various authors, is given in Table 76.

TABLE 76

RATE OF DETONATION OF TNT (m/sec)

Density of loading g/cm^2	according to Kast *[57]	according to Friedrich** [116]	according to Roth*** [117]	according to Cybulski**** [118]
0.25		2385	-	
0.56	-	3100	-	
0.83		4100	-	-
1.10		-	-	5250
1.21	-	4720	4720	
1.34	5940		-	-
1.40	-		5900	
1.45	6400		-	
1.50	6590		-	
1.52	-		7400	
1.60	6680		-	-
1.62	-	6990	-	6930

* For charges 21 mm in diameter. initiated by a 2 g detonator, in the open.

** In a metal pipe 10-15 mm in diameter.

*** Charges in bakelite pipes of 4.5-8.2 mm internal diameter.

**** In a steel pipe 31.7 mm in diameter.

Values ranging from 6900 to 7000 m/sec are usually accepted as the maximum rate of detonation of TNT.

Such outstanding advantages of TNT, its low sensitiveness to impact and friction, safe handling, considerable safety in storage (because of the low reactivity of the compound), relative safety in manufacture and relatively high explosive power, have made TNT the most widely used of all high explosives since the beginning of the twentieth century up to the present time.

As an explosive, TNT is used both compressed (in demolition charges) and in the cast form in shells and also in demolition charges. In the latter case detonators comprising compressed charges of TNT, tetryl, hexogen, or penthrite are used.

For large calibre armour-piercing shells, the sensitiveness of TNT alone is too high so it is usually diminished by adding a small quantity (1-2%) of desensitizing

or "phlegmatizing" substances such as ozokerite, bee's wax or paraffin. The last is the least efficient because of its non-polar structure. Desensitized TNT was proved to be expedient during the great naval battle between the German and British fleets at Skagerrack in 1916. The British battleships *Indefatigable, Queen Mary, Invincible, Black Prince* and *Defence*, were sunk by the fire of the German fleet which was using desensitized TNT, whereas the British shells loaded with picric acid mostly exploded on impact and failed to penetrate the armour of the German warships, causing no damage.

TOXICITY OF α– TRINITROTOLUENE

There is a considerable diversity of opinion as to the toxicity of trinitrotoluene. In Germany the substance is considered to be completely or almost completely non-toxic, while in Great Britain it is regarded as a highly toxic material. The reason for these divergent views has not been fully explained.

In the opinion of Koelsch [119], Curshmann [120], Van Duin [121], and others, pure α– trinitrotoluene is non-toxic. They consider that impurities present in TNT, such as dinitrobenzene and tetranitromethane, are responsible for any toxic effects caused by TNT. According to Koelsch, idiosyncrasy manifested by poisoning symptoms, has heen met with.

As reported in German and French official literature, the manufacture and use of TNT has not been connected with any great difficulties from the viewpoint of industrial hygiene. Nevertheless, some data indicate that cases of poisoning by TNT, sometimes fatal, have happened. Thus, in the Darmstadt district in the period between 1915 and 1918, 443 cases of poisoning by nitro compounds (mainly TNT) were registered. Among them 13 were fatal (10 women and 3 men).

The wide demand for TNT during World War I compelled factories to hasten manufacture, sometimes with insufficient regard for industrial hygiene. In some countries (e.g. Great Britain, the U.S.A.) during the 1914-1918 war numerous illnesses or even deaths of people employed in TNT manufacture, filling shells etc., were registered:

Year	Number of cases	Fatalities
1916	181	52
1917	189	44
1918	34	10

The fall in the number of poisoning cases registered in 1918, was mostly the result of introducing stricter measures and appropriate safety regulations.

The Germans (e.g. Koelsch [119]) assert that the numerous cases of poisoning that occurred in Great Britain were caused mainly because benzene was present in the toluene used for nitration, thus giving rise to the formation of dinitrobenzene.

However, the results of the investigations carried out by British physicians

do not agree with the German data. They show that chemically pure α– trinitrotoluene is as poisonous as the crude product. Finally, the view has been accepted in Great Britain that the small number of poisoning cases that occurred in Germany should be ascribed to the fact that TNT had been manufactured in Germany for many years before the World War I, so that the production processes (including safety regulations) had become well established, whereas in Great Britain TNT manufacture was something new and it was not until 1917 that the proper level of industrial hygiene was achieved in the factories and the appropriate regulations were framed.

In one of the ammunition factories in the United States, 17,000 poisoning cases, including 475 fatal cases, occurred during the first seven and a half months of World War I. They were supposed to be caused by TNT as this was a period of hasty production of ammunition. During the 20 months that followed, the number of poisoning cases fell to 7000, including 105 fatal cases.

Investigations by Legge [122] have demonstrated that the following toxic effects are produced by TNT:

(1) Irritation of the digestive tract (not differing from a similar effect produced by other agents).

(2) Methaemoglobinaemia (and the effects induced by oxygen deficiency): disturbed heart function, liver and kidney trouble and a dysfunction of the whole vascular system.

(3) A particularly harmful, effect on the liver tissues, causing severe jaundice, which in 25-30% of cases may end in death.

(4) Aplastic anaemia, manifesting itself by a fall of the number of red and white corpuscles, caused by the dysfunction of the bone marrow. Almost all of these cases end in death.

As Moore [123] believes, poisoning can occur when TNT is absorbed through the skin.

In 1918 a special medical committee in Great Britain published a statement on TNT poisoning. The committee believed that disturbances in the digestive tract are not decisive symptoms, and if caused by other factors may lead to wrong conclusions. Yellow stains on the skin, usually appearing when working with TNT, are not indubitable symptoms of poisoning. The presence of trinitrotoluene in the urine (Webster's test [124]) should not be considered as a proof of poisoning. The real symptoms are :

(1) Paleness of face, a grey colour of lips, which disappears upon excitation. Sometimes the lips and the tongue may even be a violet colour.

(2) Stomach ache, characteristically localized.

(3) Constipation and flatulence.

If no jaundice has appeared, the treatment is simple, and the prognosis is good. The treatment should consist in:

(1) Isolation of the patient from contact with TNT and allowing plenty of fresh air.

(2) Staying in bed for one or two days.

(3) A special diet, consisting of milk, milk dishes, fruit and vegetables, and beverages such as tea and coffee.

Where jaundice occurs clinical treatment is necessary. The patient should be given milk, starting with small portions increasing to one liter daily.

Young people are far more liable to TNT poisoning than adults. For the first four working weeks some people exhibit a considerable resistance to poisoning, others fall ill within the fifth and the fifteenth week of work.

Here are the principal precautionary measures which should be strictly observed.

(1) The age of workers in TNT factories should not be below 18 years.

(2) All workers should be submitted to medical examination before starting work, and subsequently should be examined every week.

(3) Workers should be protected against dust, and as far as possible against skin contact with TNT. Working places should be adequately ventilated.

(4) Special working clothes put on in the changing room. They should fit tightly at the wrists, and neck, to prevent the penetration of dust. Hair should be covered with a cap or other form of protective head dress. This protective clothing should be washed every week.

(5) Personal cleanliness is imperative. All workers should wash before meals and before going home.

(6) Before starting work they should drink a pint or so of milk. Eating fresh vegetables should be recommended.

(7) Workers in TNT factories should be transferred periodically to other work, out of contact with TNT.

Norwood [124a] suggested using a special liquid soap to remove TNT from the skin. The liquid soap should contain 5-10% K_2SO_4 and 5-10% of a wetting agent.

There is no doubt that TNT is toxic to man. Experience gathered in the World War II has supplied statistical data which confirm this. Branslavljevic [125] gives the following data. Out of 66 workmen employed in a Yugoslavian factory in the section where ammunition was filled with TNT, 42 persons showed symptoms of poisoning such as cyanosis, pallor and jaundice.

Liver damage was confirmed in 19 workmen, another 19 suffered from anaemia, and in 5 a combination of both conditions was found.

Crawford [126] recorded 24 cases of aplastic anaemia in Great Britain, all of them the result of exposure to TNT during World War II.

Statistical data referring to the World War II reported for some thousand mild cases of poisoning by TNT in the U.S.A. apart from 379 more serious cases and 22 fatal ones. Eight men died of toxic hepatitis, 13 of aplastic anaemia and 1 of a combination of both (McConnell and Flinn [127]). The same authors reported that at a TNT dust concentration in the air amounting to 3 mg/m^3, distinct poisoning symptoms were observed. According to these authors, the maximum permissible concentration of TNT in the air is 1.5 mg/m^3.

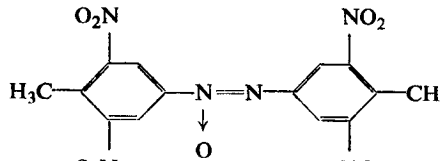
An important observation made by Larionovi [128] was that TNT, present in waste waters in a concentration of 25-80 mg/l., lowered the oxygen consumption of bacteria by 5-30% possibly because it inhibited their activity. In addition, TNT has been found toxic to some seaweeds and to fish.

According to Kratz [129], 1 mg of TNT in 1 l. of water kills fish. Seifert [130] reported that the lethal dose for fish was 2 mg of TNT in 1 1. of water, while a concentration of 0.15 mg TNT/l. might be lethal to plankton which form the principal nourishment for fish. For this reason the problem of decontamination of waste water from TNT manufacture is of primary importance (see further, p. 390).

METABOLISM OF TRINITROTOLUENE

Detailed studies on the metabolism of trinitrotoluene in the human body and in animals were carried out during World Wars I and II. They have since been published.

Voegtlin, Hooper and Johnson [131] reported that trinitrotoluene was reduced to dinitrotoluidine of an unknown structure, and to tetranitroazoxytoluene, the constitution of which was given later by Dale [132] :

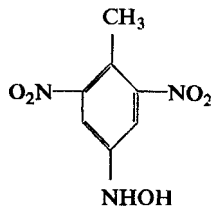


I

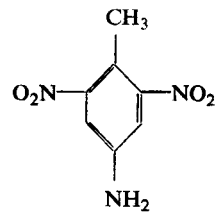
This compound can be found in urine.

Extensive studies on the metabolism of α– trinitrotoluene in man and animals have been published by Channon, Mills and R. T. Williams [133]. The authors were able to prove that tetranitroazoxytoluene was not present in fresh urine, but was found as a product of an in vitro reaction between various products of metab olism.

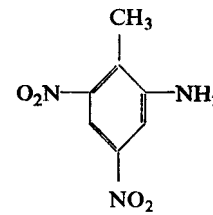
The following amines and hydroxylamines were isolated from the urine of animals receiving TNT :



I I

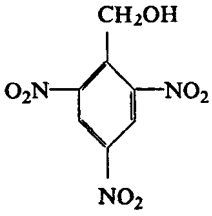


III

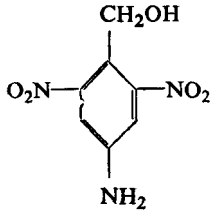


IV

The azoxy compound is presumably formed during the oxidation of product II. In addition, oxidation products and oxidation-reduction products are formed:



V



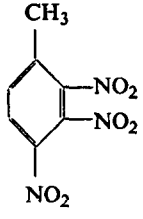
VI

Compound II is highly toxic. It results in the formation of methaemoglobin. The presence of trinitrotoluene in the human body leads to an enhancement of the formation of glucuronic acid, which reacts with the alcohols V and VI to form the corresponding esters.

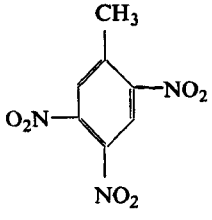
The formation of the amines III and IV has also been observed by Lamberg and Callaghan [134].

UNSYMMETRICAL ISOMERS OF TRINITROTOLUENE

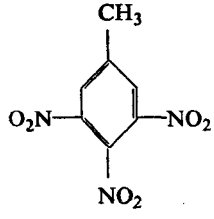
The following unsymmetrical trinitro derivatives of toluene are known:



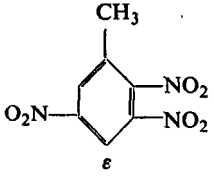
β
2,3,4-
m.p. 112°C



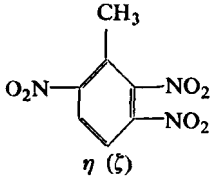
γ
2,4,5-(3,4,6-)
m.p. 104°C



δ
3,4,5-
m.p. 137°C



ε
2,3,5-
m.p. 97.5°C



η (ζ)
2,3,6- (2,5,6-)
m. p. 111°C

All isomers are formed by nitration of *m*- nitrotoluene. Hepp [35] isolated the β– and γ– isomers from the product of a severe nitration of *m*- nitrotoluene. Their structures have been determined by Will [37].

In a number of detailed investigations Marqueyrol, Koehler and Jovinet [135,

136, 137] and their colleagues found that the η– isomer is also formed during the nitration of *m*- nitrotoluene. Attempts to find the δ– and ε– somers in the products of nitration of *m*- nitrotoluene were originally unsuccessful. These compounds were obtained by an indirect method. Later de Beule [31] succeeded in obtaining all isomers by nitrating *m*- nitrotoluene. His results are summarized in the diagram (p. 328). The composition of crude TNT is according to de Beule: 95.1% of α– isomer, 1.36% of β–, 2.69% of γ–, 0.002% of δ–, 0.29% of η– and 0.009% of ε– isomer, and also unchanged 2,3-, 2,5- and 3,5-dinitrotoluenes in quantity of 0.33, 0.15 and 0.06% respectively.

The nitration of *m*- nitrotoluene was also studied by Brady and his co-workers [136-139] and by Drew [140].

PHYSICAL PROPERTIES

The physical properties of the unsymmetrical isomers of trinitrotoluene are similar to those of α– trinitrotoluene. They are crystalline substances of a pale yellow colour, soluble in most organic solvents, insoluble in water and non-hygroscopic.

THERMOCHEMICAL PROPERTIES

Heat of crystallization. Garner and Abemethy [3] found the following values for the heats of solidification of the β– and γ– isomers:

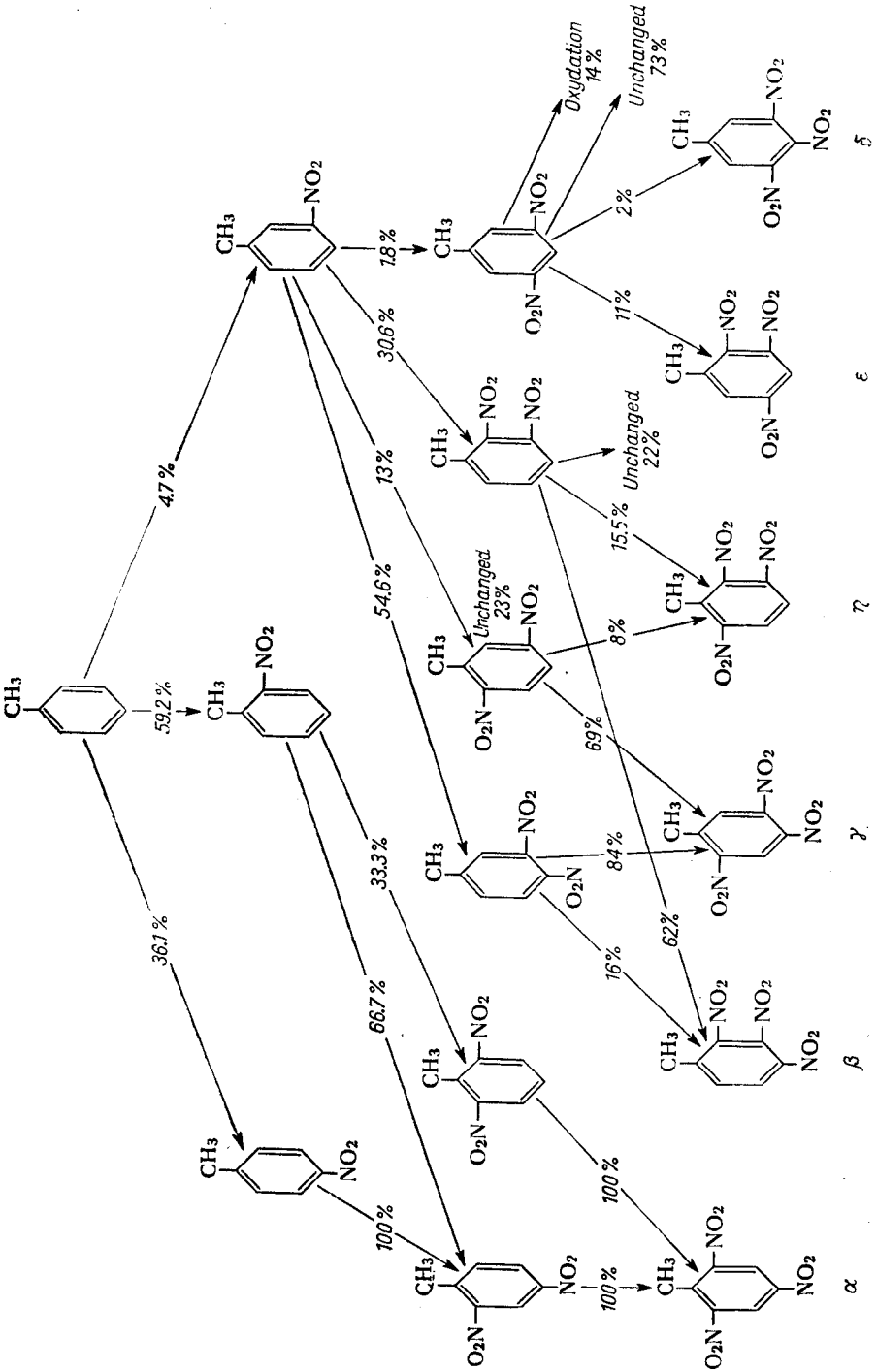
β– trinitrotoluene 5.0 kcal/mole
γ– trinitrotoluene 5.4 kcal/mole

Heat of combustion and heat of formation. The same authors give the following values for unsymmetrical trinitro derivatives of toluene (Table 77).

TABLE 71

HEATS OF COMBUSTION AND FORMATION OF UNSYMMETRICAL ISOMERS OF TRINITROTOLUENE

Isomer	Heat of combustion (at constant volume) with a correction for nitric acid kcal/mole	Heat of formation (for amorphous carbon), kcal/mole
β– trinitrotoluene	834.1	+16.9
γ– trinitrotoluene	827.4	+24.2
δ– trinitrotoluene	829.9	+21.7
ε– trinitrotoluene	825.6	+26.0
η– trinitrotoluene	827.1	+24.5



Isomers formed on nitration of toluene according to de Beule.

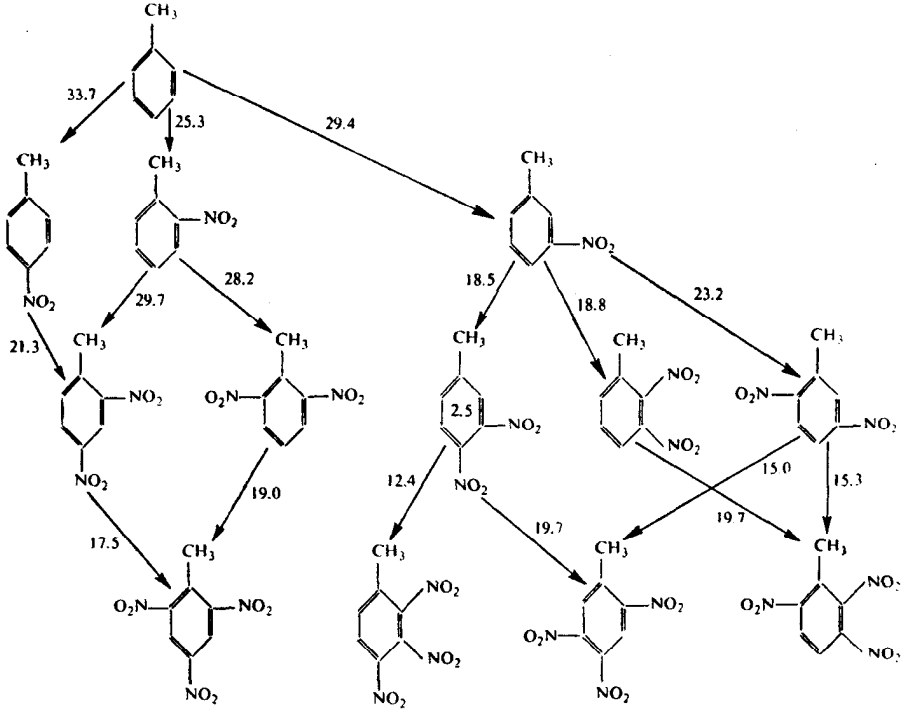
Heat of nitration. Heats of direct conversion of dinitrotoluenes to trinitrotoluenes are listed in Table 78 (after Gamer and Abemethy [3]).

TABLE 78

HEATS OF NITRATION OF DINITRO- TO TRINITRO-TOLUENE

Starting compound	Product	Heat, kcal/mole
3,4-Dinitrotoluene	2,3,4-trinitrotoluene	12.4
	2,4,5- (3,4,6) „	19.7
2,3 „	2,3,4- „	12.1
	2,3,6- „	19.7
2,5 „	2,4,5- (3,4,6-) „	15.0
3,6 „	2,3,6- „	15.3

SCHEME OF NITRATION OF TOLUENE*



The figures accompanying the arrows indicate heats of reaction, in kcal/mole.

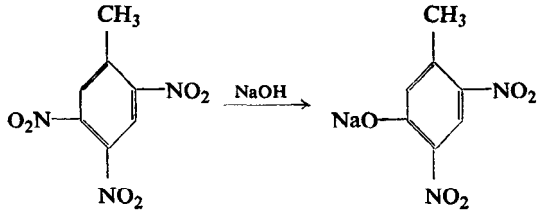
CHEMICAL PROPERTIES

The chemical properties of the unsymmetrical isomers of trinitrotoluene are in some respects similar to those of α– trinitrotoluene, e.g. they are not affected by acids. However, they differ from α– trinitrotoluene as their nitro group, located

in the meta position to the CH_3 group, is rather mobile as it is in the *ortho* or *para* position to other nitro groups. Such mobile nitro groups are easily substituted. Here are the characteristic reactions, as shown by the most important γ– isomer.

Reactions with alkalis

The unsymmetrical isomers of trinitrotoluene readily react with aqueous solutions of sodium or potasium hydroxide, forming salts of dinitrocresol (Will [37]):

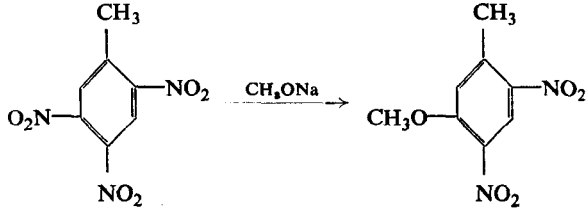


(25)

The reaction can take place at room temperature. The reaction with sodium carbonate at a temperature corresponding to the boiling point of alcohol, occurs in a similar way.

Brady [137] found that a concentrated solution of sodium acetate acted on unsymmetrical trinitrotoluene in a way similar to the action of weak alkalis, giving the corresponding dinitrocresols. Under such conditions less ill-defined amorphous products were obtained than in the reaction with strong alkalis, where they were formed in great quantities.

Under the influence of an alcoholic solution of sodium- or potassium methoxide or ethoxide one of the nitro groups may be replaced by the methoxy or ethoxy group :



(26)

Sodium hydroxide gives the following colour reactions with the unsymmetrical isomers of trinitrotoluene (Table 79).

TABLE 79

COLOUR REACTIONS OF THE UNSYMMETRICAL ISOMERS OF TRINITROTOLUNE WITH SODIUM HYDROXID E

Isomer	Sodium hydroxide	
	in acetone solution	in alcohol-acetone solution
β	violet, bright	green, bright
γ	violet-greyish	blue with a violet tinge
η	light pink	red

Ammonia gives similar colour reactions.

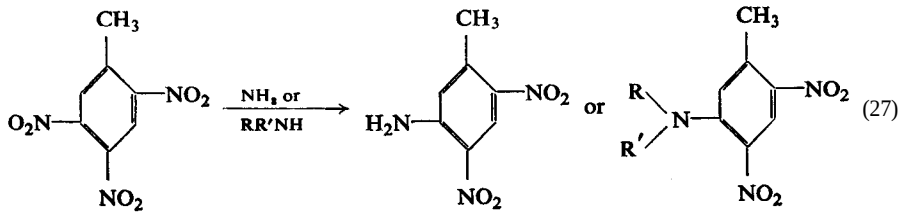
The unsymmetrical isomers of trinitrotoluene also give specific reactions with sodium carbonate and with lead oxide. The former also affects the ignition temperatures of the isomers. The corresponding data are tabulated below, in Table 80 (after Brunswig [141]).

TABLE 80

SPECIFIC REACTIONS OF THE UNSYMMETRICAL ISOMERS OF TRINITROTOLUENE WITH Na_2CO_3 AND PbO

Isomer	Reaction with boiling alcohol solutions		Ignition temperature, °C	
	Na_2CO_3	PbO	Pure isomer (0.29)	Compound (0.75 g) with some quantity of Na_2CO_3 (0.05 g)
α	forms brown salts (addition products)	no change	290	231
β	readily forms sodium dinitrocresolate	forms lead dinitk-cresolate	302	211
γ	,,	,,	291	194
δ	,,	,,	313	252
ε	some sodium dinitro-cresolate is ob-tained, being formed very slowly	reacts only with great difficulty	332	249
η	sodium dinitro-cresolate is formed	lead dinitrocresolate is formed	335	269

Reactions with ammonia or with amines lead to the formation of dinitrotoluidine or its N-substituted derivatives:

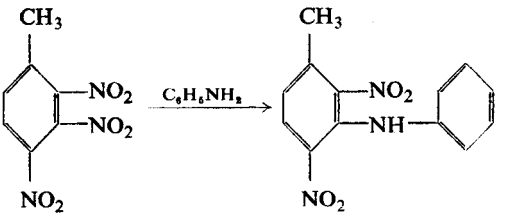


(27)

The reaction with ammonia in an alcoholic solution may proceed both in the hot and in the cold (Hepp [35]; Giua [46]). It may be utilized for the identification

of amines (Brown and Campbell [142]). It has also been utilized for determining the structure of unsymmetrical isomers of trinitrotoluene (p. 336). The isomers react with hydrazine and phenylhydrazine in a similar way.

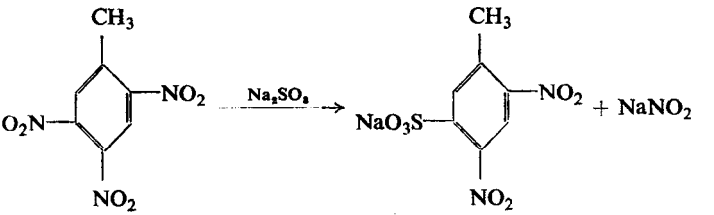
Brady, Hewetson and Klein [139] studied the action of aromatic amines on unsymmetrical trinitrotoluene. They obtained diphenylamine derivatives, e.g. :



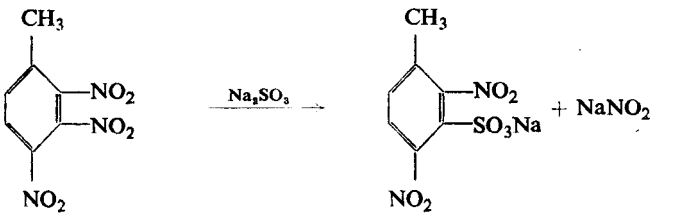
(28)

Reaction with sodium sulphite

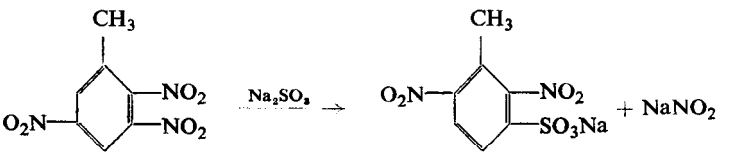
This reaction is of great practical importance, since it is the simplest and most frequently used way of removing the unsymmetrical isomers from crude TNT. The reaction involves the following transformations, taking place at room temperature:



(29a)



(29b)

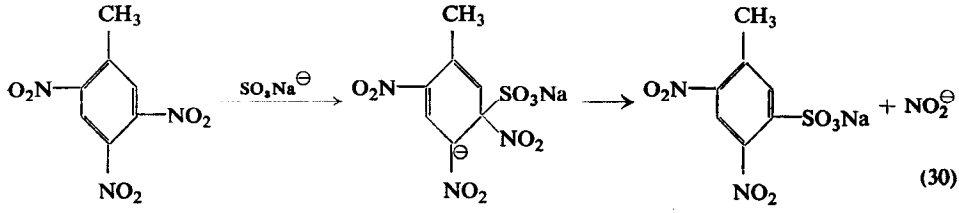


(29c)

The solution of sodium dinitrotoluenesulphonates formed is of a characteristic light red colour. The reaction is carried out using either a 2-3% solution at a temperature of 70-80°C or a 6-8% solution at room temperature to 30°C.

Brady, Hewetson and Klein [139] tried to elucidate the mechanism of the reaction of sulphitation of unsymmetrical trinitrotoluenes. They assumed the formation of an addition product of sodium sulphite and the nitro compound in the first stage.

This is a nucleophilic reaction, and its mechanism, according to the author of the present book, may possibly be represented as follows:



(30)

The reaction was first mentioned by Laubenheimer [143] when examining chloro-3,4-dinitrobenzene. However for a long time no notice was taken of the possibility of putting it into practice. It was only during World War I that the method was introduced in the U.S.A., and this happened quite accidentally. In the search for methods of removing unsymmetrical isomers from crude TNT, the reduction of trinitrotoluenes was studied. It was hoped that the nitro group in the meta position, being chemically more active, would be more easily reduced, and that the reduction product would be relatively soluble in water. Sodium polysulphide was used for the reduction. However, it was found that the product of the reaction was strongly contaminated with sulphur formed at the reaction. Among other reducing agents used, sodium sulphite was shown to be a very efficient one in removing unsymmetrical isomers, its action consisting, however, not in the reduction of the nitro group, but its replacement by a sulpho group.

As Muraour [103] found, the reaction of sodium sulphite was not confined to unsymmetrical trinitro derivatives of toluene. α– Trinitrotoluene also reacted with Na_2SO_3 to form dinitrotoluene sulphonic acid, the difference lying in the fact that the reaction proceeds much more slowly than with unsymmetrical isomers. A 3% solution of Na_2SO_3, acting for 1 hr, dissolves at room temperature about 1% of α– trinitrotoluene.

According to the British literature of World War I, the optimum temperature of sulphitation is 40-45°C. At higher temperatures α– trinitrotoluene reacts too vigorously, which results in a certain loss of the product. On the other hand, the action of sulphite on the unsymmetrical isomers at lower temperatures is too slow.

Since solutions of sodium sulphite are alkaline, which affects TNT unfavourably, a number of workers have developed other methods consisting in lowering the pH of the sodium sulphite solution by adding buffers.

Thus G. P. Davies [144] suggested the use of the Na_2SO_3 solution with such buffers as mono- and di-sodium phosphates or boric acid, which reduce the pH to 7.0-8.3.

In industrial practice, losses of crude TNT in the sulphitation process amount from 6 to 8%. Out of this 2%-3.5% is ascribed to the loss of α– trinitrotoluene and 3.5-4.5% to that of unsymmetrical isomers and other impurities, such as tetranitromethane (p. 339) and trinitrobenzene which is easily soluble in sodium sulphite, forming addition products.

Muraour observed the important fact that trinitro-m-xylene reacts with sodium sulphite only with great difficulty, while trinitromesitylene does not react with it at all. Tetranitromethane, which is a common impurity of TNT, reacts with sodium sulphite to yield a water-soluble salt of sulphonic acid (p. 339).

After sulphitation, the setting point of TNT rises on the average by 2.2°C (e.g. from 78.0°C to 80.2°C).

Barbiere [145] examined quantitatively the process of sulphitation of α–, β– and γ– trinitrotoluenes using a 6% solution of Na_2SO_3 at different temperatures (30-60°C) and in another series of experiments the influence of the concentration of sodium sulphite solution on the solubility of the isomeric trinitrotoluenes at 30°C. He also determined:

(a) the total solubility of α– trinitrotoluene (S_1) which includes both the formation of the soluble addition compound and sodium salts of nitrosulphonic acids;

(b) the "irreversible" or "real" or permanent solubility (S_2) which is caused only by formation of sodium salts of nitrosulphonic acids.

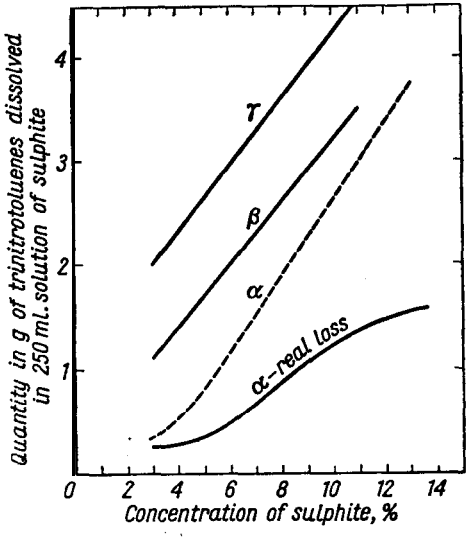


FIG. 75. Influence of the concentration of sodium sulphite solution on solubility of α–, , β– and γ– trinitrotoluene (Barbiére [146a]).

This was determined by diluting the solution to hydrolyse the addition compounds. Precipitation of recovered α– trinitrotoluene gives the "transient" solubility (S_3). By definition $S_2 = S_1\text{-}S_3$.

Some of Barbiére's results are given in Fig. 75. Here both the total and real solubility of α– trinitrotoluene are shown.

D. Smolenski and Plucinski [146] made a thorough study of the sulphitation of *a*-, β– and γ– trinitrotoluenes. Some of their results are summarized diagrammatically in Fig. 76 which illustrates the influence of sulphitation temperature on total,

permanent and transient solubility of a-trinitrotoluene in solutions of sodium sulphite of different concentrations. The trend of the curves is similar to that found earlier by Barbiére [145].

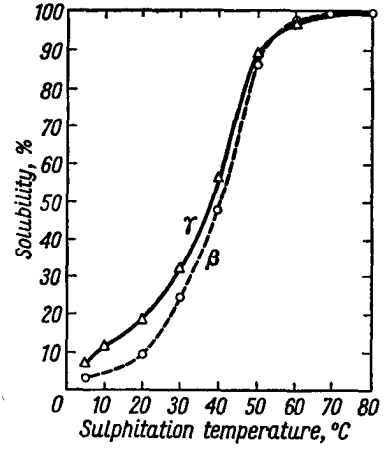


FIG. 76. Influence of the temperature of sulphitation on the solubility of α– trinitrotoluene at different concentrations of sodium sulphite (Smolenski and Plucinski [146]).

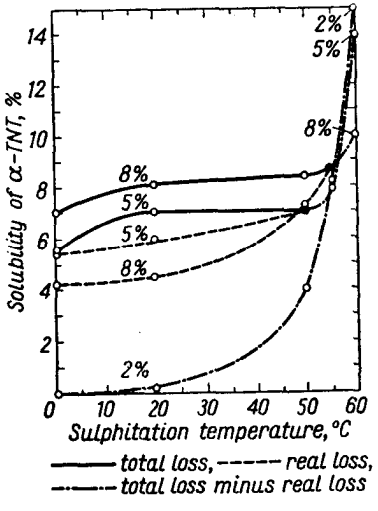


FIG. 77. Influence of the time of sulphitation on the solubility of a-trinitrotoluene at different temperatures and constant concentration (4%) of sodium sulphite (Smolenski and Plucinski [146]).

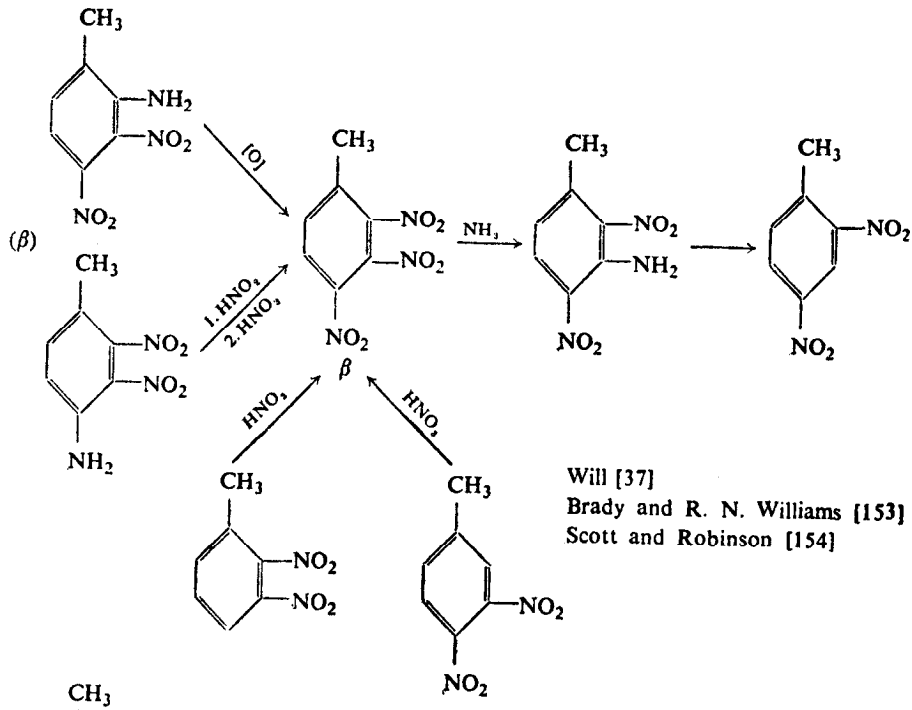
The influence of the time of sulphitation on the solubility of β– and γ– trinitrotoluene at different temperatures according to D. Smolenski and Plucinski [146] is given on the Fig. 77.

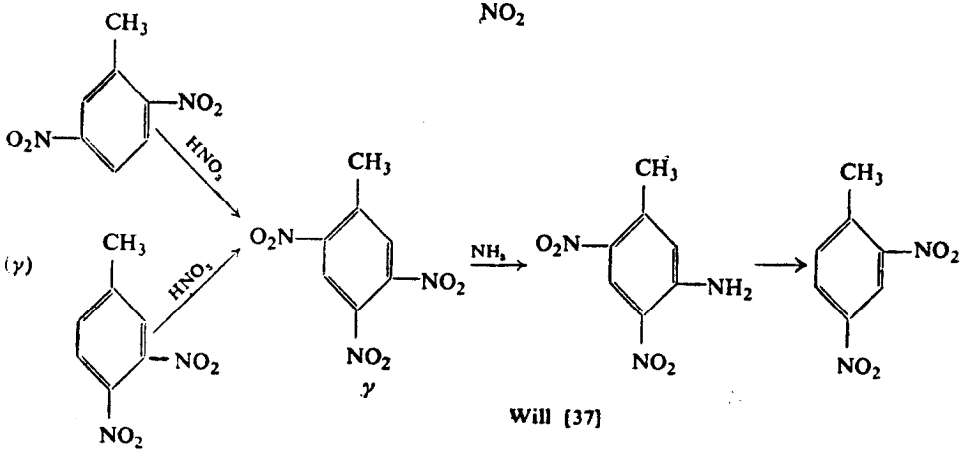
Effect of light

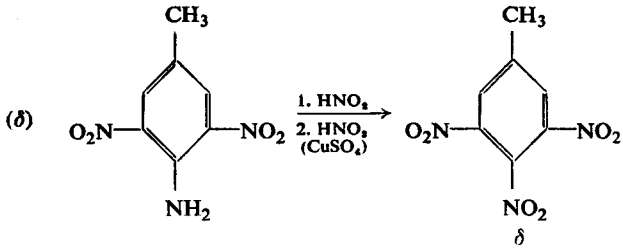
The unsymmetrical isomers of trinitrotoluene are affected by light in an apparently similar way, as in the instance of α– isomer, turning brown on exposure to sun. However, the chemical nature of the process has not been investigated.

PREPARATION AND CONSTITUTION OF UNSYMMETRICAL TRINITROTOLUENES

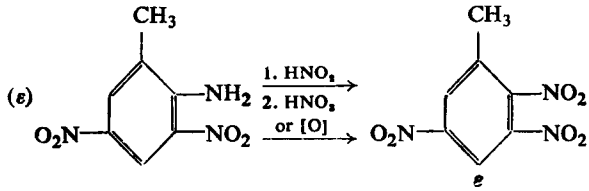
The following reactions give an indication of structure and the mode of preparation of the isomers:



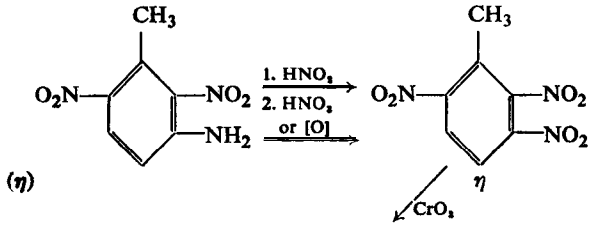




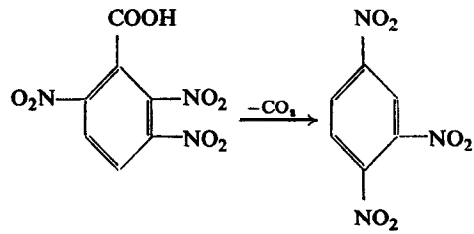
Körner and Contardi [155]



Körner and Contardi [156]
Brady and R. N. Williams [153]



Körner and Contardi [158]
Brady and Taylor [136]



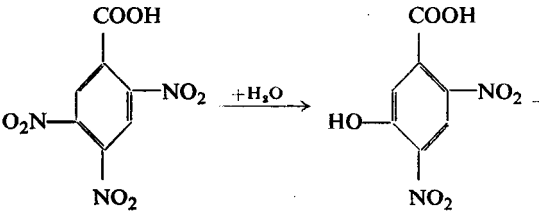
OTHER BY-PRODUCTS IN THE NITRATION OF TOLUENE

Apart from the unsymmetrical isomers of trinitrotoluene, other by-products are formed in the nitration process, owing to oxidation or decomposition processes.

Oxidation leads to the formation of di- and tri-nitrocresols, impurities frequently met with in TNT. Nitrocresols are mainly formed during the nitration of toluene to mononitrotoluene (Noelting and Forel [11]). If they have not been removed from mononitrotoluene by washing with alkalis, they undergo either further nitration to trinitrocresol, or oxidation to oxalic acid. Trinitrocresol may be removed from TNT by mild alkali washing (e.g. with a $NaHCO_3$ or a sodium sulphite solution).

During the trinitration the methyl group is oxidized to the carboxyl group. The trinitrobenzoic acids behave in different ways in the course of hot washing of crude TNT. Thus 2,4,6-trinitrobenzoic acid is readily decarboxylated and

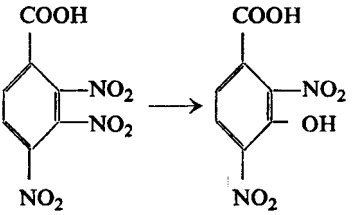
sym-trinitrobenzene results (p. 254). According to Schmidt [147], 2,4,5-trinitrobenzoic acids gives rise to hydrolytic denitration to yield 2,4-dinitro-5-hydroxybenzoic acid (I).



(31)

I

It is probable that 2,4-dinitro-3-hydroxybenzoic acid (II) can also be formed in the similar way :



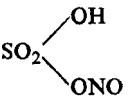
(32)

II

Also hydroxy-2,4,6-trinitrobenzoic acid (III) can be present among the other by-products in the formation of trinitrotoluene.

Hydroxynitro acids (I), (II) and (III) are (according to Schmidt) washed from the crude TNT and are present in the wash-waters. Trinitrobenzoic acids remain in TNT as impurities. The trinitrobenzoic acids formed are readily decarboxylated. CO_2 is evolved and only trinitrobenzenes remain in TNT as its impurities.

As a consequence of the strong oxidation processes occurring mostly during the trinitration (naturally at the expense of nitric acid) a relatively large quantity of nitrous acid is formed, which in sulphuric acid medium gives nitrosyl sulphuric acid :



or $[HSO_4]^{\ominus}[NO]^{\oplus}$

According to Kobe and Lakemeyer [17], the nitrosylsulphuric acid represents about 17 wt. % of the total amount of spent acid from the trinitration. Its presence would subsequently considerably affect the process of the nitration of toluene to the mononitro-product, since it makes 14-17 wt. % of the acid used for the mononitration.

According to Gorst [2], the rate of the oxidation reactions falls with increase in the value Φ, or in other words with the increase of concentration of H_2SO_4 in the nitrating mixture or in the spent acid. A diagram (Fig. 102) related to nitration of dinitroxylene is given on the (p. 396).

Sapoihnikov (according to Gorst [2]) established that the losses of nitric acid during the nitration of DNT to TNT amount to 70-75% due to oxidation processes, the rest (25-30%) being due to evaporation of nitric acid.

Complete decomposition resulting from a vigorous nitration (with the loss of ca. 5% of toluene) may lead to the formation of the products: NH_3, CO, CO_2, etc. [158] (p 76).

Reduction products of nitric acid, such as nitrogen and nitrogen oxides can also be formed as the result of oxidation processes. Niederer [148] found that N_2 and NO were not formed in the nitration of nitro- to dinitrotoluene, while they were present in the nitration products of di- to tri-nitrotoluene. In addition to nitrogen and nitrogen oxide, carbon mono- and dioxide were formed in the last stage of nitration. Their amount and the CO to CO_2 ratio increased with temperature.

According to Eastman [158] the percentage of CO may be sometimes so high as to cause a gas explosion in the nitrator.

The break-down of the molecule, and the loss of the methyl group, may lead to the formation of tetranitromethane during the nitration process. This substance is always encountered in TNT as an impurity, and its presence can be established by its characteristic smell reminiscent of that of nitrogen oxides.

It has been suggested that tetranitromethane increases the sensitiveness of TNT to impact, friction and high temperature. That is, why the removal of this impurity is very advisable, the more so because in the course of time it transforms into nitroform, $CH(NO_2)_3$, an acid substance readily yielding salts which are sensitive to thermal and mechanical stimuli. The simplest way of removing tetranitromethane consists in treating it with sodium sulphite, which reacts in the following way:

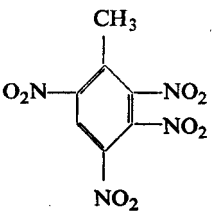
$$C(NO_2)_4 + Na_2SO_3 \rightarrow C(NO_2)_3SO_3Na + NaNO_2 \qquad (33)$$

The sodium salt of trinitromethanesulphonic acid is readily soluble in water. It is unstable and, according to Muraour [103], undergoes further hydrolysis:

$$C(NO_2)_3SO_3Na + H_2O \rightarrow CH(NO_2)_3 + NaHSO_4 \qquad (34)$$

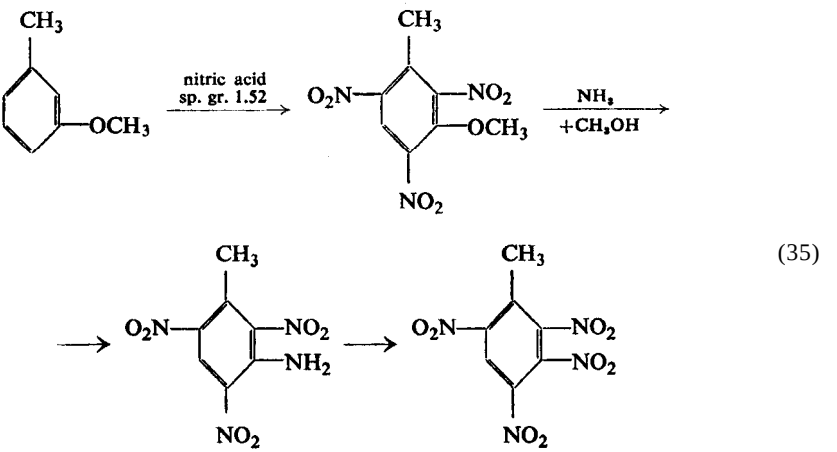
According to Kostevitch [159] tetranitromethane can be responsible for the formation of “tarry matters“.

TETRANITROTOLUENE



m.p. 136.5°C

The compound cannot be obtained by direct nitration of trinitrotoluene. It was first obtained by Holleman [149] from the methyl ether of *m*- cresol:



(35)

The starting product is nitrated with anhydrous nitric acid (sp. gr. 1.52) to the trinitro compounds. The methoxy group of the latter, on boiling with ammonia in methyl alcohol, can be substituted by an amino group.

The trinitro-m-toluidine thus obtained is oxidized in sulphuric acid solution with potassium persulphate. The yield of this stage of the reaction is about 85% of theory. The tetranitrotoluene thus prepared may then be recrystallized from nitric acid of a sp. gr. of 1.40.

Tetranitrotoluene is much more stable than tetranitrobenzene. It is considerably. more resistant to hydrolytic action of water. At room temperature the presence of trinitrocresol cannot be detected earlier than 24 hr; at 80°C only 57% of the product is converted within this period.

Holleman reported the following explosive properties of tetranitrotoluene :

Lead block test	327 cm^3
Sensitiveness to impact (2 kg falling weight)	50 cm

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CHAPTER IX

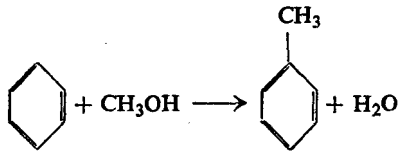
TNT MANUFACTURE

TOLUENE

TOLULENE is the principal raw material for the manufacture of TNT. It is produced from light oil and from the gases obtained by the dry distillation of coal.

In some oil producing countries (e.g. U.S.S.R.), toluene is obtained from aromatic fractions of petroleum or by aromatization of heavy petroleum hydrocarbons by cracking processes (in Poland studies on aromatization of petroleum were carried out by K. Smolenski [1] between 1922 and 1939). In war-time the demand for toluene for nitration was so large, that these two sources were inadequate. During World War II new methods of toluene manufacture on an industrial scale were developed starting from benzene and methyl alcohol and from n-heptane.

The reaction of toluene formation from benzene and methyl alcohol can be represented by the following scheme:



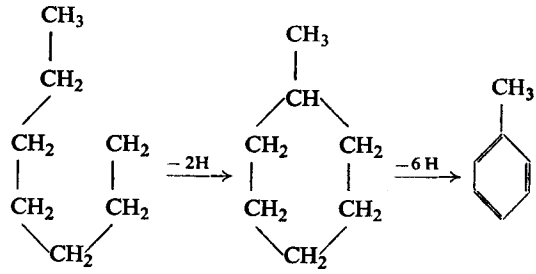
(1)

The reaction proceeds at a temperature of 340-380°C and at pressure of 30-35 atm in the presence of zinc diphosphate on silica catalyst.

Since under these conditions higher homologues of toluene (xylenes, etc.) can readily be formed, a large excess of benzene is used for the process. The yield of toluene obtainable by this method (calculated on methyl alcohol) is close to the theoretical one.

In Germany, during World War IL nearly 4000 tons of toluene were produced monthly by this method.

The method of preparation of toluene from n-heptane was mainly developed in the U.S.A. It is based on the following reaction:



(2)

It is carried out at 480-530°C at a pressure of 15 atm in the presence of a Cr_2O_3 + + MoO_3 catalyst, on a Al_2O_3 or MgO carrier. The yield obtained amounts to 72% of the theoretical.

Crude toluene obtained by this method contains 3-5% olefins, so it must be purified by refining with sulphuric acid, followed by washing with water and distillation.

Toluene for nitration must be of high purity, in fact almost chemically pure. The boiling range of the product should be 109-111°C, with at least 95% distilling within a range of 1°C. The specific gravity should be 0.870±0.002 at 15°C.

Only an insignificant amount of unsaturated aliphatic hydrocarbons is admissible in toluene for nitration. They may be detected by shaking a sample with concentrated sulphuric acid. If the toluene is pure, the sulphuric acid separates very quickly as a colourless or slightly yellow ("straw yellow") lower layer. If unsaturated hydrocarbons are present in significant quantities a stable emulsion is often formed, and the sulphuric acid turns brown or even black. Such a product cannot be used for nitration.

Nowadays an infra-red spectrophotometric technique is usually applied in testing toluene for purity (Gore and Patberg [2]).

It should be noted that toluene purity cannot be assessed by the ultra-violet technique, since strong bands produced by toluene (as about 262 mμ) mask those that may be produced by olefins.

Toluene obtained from petroleum should contain no more than 4% of paraffinic hydrocarbons. The content of the latter is determined by sulphonation of the toluene with concentrated sulphuric acid or with 20% oleum. Sulphonated aromatic compounds are washed out with water to leave the paraffin hydrocarbon which is not affected by oleum.

If the toluene contains a higher proportion of paraffinic hydrocarbons it can still be nitrated, provided the mononitration product is subjected to distillation (preferably with steam) to remove saturated hydrocarbons. According to Desseigne, Gladel, Guillemin and Sousselier [3], toluene containing 30-40% of saturated hydrocarbons can be treated in this way to obtain nitrotoluene suitable for further nitration.

The U.S.S.R. specification (OST 464) for nitration grade toluene requires the following properties (Table 81):

TABLE 81

	Toluene from coal	Toluene from petroleum
Specific gravity at 15°C	0.870±0.002	0.863-0.870
Boiling range	109-111°C (95% distils within a range of 1°C)	108.5-111°C
Colouration with sulphuric acid (comparison with standard potassium dichromate solutions of concentrations x grammes per 1 l. of 50% sulphuric acid)	x 0.5	x 0.5
Bromine number (y grammes of bromine decolourized by 100 ml. of toluene)	y 0.8	y 0.8
Sulphonation test with 5% oleum	-	not less than 96 vol. % should be sulphonated

According to a German standard, toluene for nitration shall distil within a range not wider than 0.8°C.

NITRATION OF TOLUENE TO TNT

GENERAL REMARKS

The nitration of toluene to TNT is carried out by successive introduction of nitro groups. Such a method is justified from the points of view both of safety and economy as it permits the most efficient use of acids and produces a final product of high purity due to the purification of the intermediate products obtained in the separate stages of the process.

Nitration is commonly carried out in three stages, and less often in two Stages.

The principle of economical acid usage is simply achieved by using the spent acid from a higher nitration stage for the lower stage, after it has been fortified to the required concentration.

The diagram presented below illustrates the reactions occurring, and shows the average composition of the products and heat effects of the reactions. Another diagram (Gorst [4]) gives the yields of nitration of intermediate compounds.

THREE-STAGE PROCESS FOR MANUFACTURE OF TNT'

The three-stage nitration of toluene to TNT comprises the following processes:

$$\text{I.}\quad C_6H_5.CH_3 \rightarrow C_6H_4.CH_3.NO_2 \quad \text{(MNT)}$$

$$\text{II.}\quad C_6H_4.CH_3.NO_2 \rightarrow C_6H_3.CH_3.(NO_2)_2 \quad \text{(DNT)}$$

$$\text{III.}\quad C_6H_3.CH_3.(NO_2)_2 \rightarrow C_6H_2.CH_3.(NO_2)_3 \quad \text{(TNT)}$$

OLD FRENCH PROCESS

This process, as described by Pascal [5], was used in France both during World War I and in the early period of time between the two wars. Separate operations in the three-stage nitration process are carried out in the following way:

Nitration of toluene to MNT ("mononitration"). To introduce one nitro group into toluene a mixture of acids is used (sp. gr. 1.672) of composition:

HNO_3	28%
H_2SO_4	56%
H_2O	16%

Toluene (650 kg) is run into a nitrator, and 1580 kg of the nitrating mixture is added with vigorous stirring. The temperature in the nitrator should be maintained at 40°C by using a cooling jacket and a coil situated inside the nitrator. After the reagents have been mixed thoroughly the temperature of the mixture should be raised to 60°C and maintained then for 45 min to 1 hr. When the reaction has been completed the nitrator contents are cooled to room temperature and the stirrer is stopped. The liquid is allowed to stand still until quiet, and then the lower layer, i.e. the spent acid, is drained off.

The composition of the spent acid (sp. gr. 1.66) is:

HNO_3	trace
H_2SO_4	69%
H_2O	29%
NO_2	2%

From 650 kg of toluene 910-950 kg of MNT is obtained, i.e. 140-146 kg for 100 kg of toluene. Since the theoretical yield is 149 kg of MNT for 100 kg of toluene, the actual yield amounts of 94-98% of theory. Losses are due mainly to dissolution of the nitration product in the spent acid (up to 4.5% of the total amount of nitrotoluene).

Nitration of MNT to DNT ("dinitration"). The acid from the first stage of nitration, composed of:

HNO_3	32%
H_2SO_4	61%
H_2O	7%

is run into MNT over a period of 2 hr, with constant stirring. The amount of the acid should correspond to a 45% excess of HNO_3. During stirring the temperature should be maintained at 40°C for the first hour and at 50°C for the next hour.

When all the acid has been run into the nitrator the mixture is heated to 90°C and maintained at this temperature for half an hour. Then the nitrator contents are cooled to 60-65°C, i.e. to a temperature at which crude DNT remains liquid (m. p. 56-58°C).

Spent acid from dinitration has the composition:

HNO_3	2.5%
H_2SO_4	76.0%
H_2O	20.0%
NO_2	1.5%

DNT, being lighter than the spent acid (sp. gr. at 60°C - 1.337, at 80°C - 1.318) rises to the surface. The spent acid is drained off and DNT, while still hot, is run into a vessel with concentrated sulphuric acid.

From 100 kg MNT 130 kg of DNT are obtained (the theoretical amount is equal 133 kg), hence the yield amounts to 98% of the theoretical. When calculated on toluene, 188 kg of DNT are obtained from 100 kg of toluene (theoretically 198 kg), which corresponds to 95% of the theoretical yield.

Nitration of DNT to TNT ("trinitration"). An anhydrous mixture of acids is used for the third stage of nitration. Mixture of the composition

HNO_3	49%
H_2SO_4	49%
NO_2	2%

is run into the nitrator where it is heated to 80-90°C. Then the DNT from the preceding stage of nitration dissolved in concentrated sulphuric acid in 1: 1 weight ratio is added with stirring. Prior to mixing, the solution is heated to 60°C.

The resultant composition of the nitrating mixture is:

HNO_3	19%
H_2SO_4	80%
NO_2	1%

1500 kg of it are used for 1000 kg of DNT, this being one charge.

The two solutions are stirred for about 2 hr during which time the temperature of the liquid should rise to 105°C. The nitrator contents are then heated up to 120°C, and this temperature is maintained for one hour and a half.

In consequence of such drastic conditions of nitration several side reactions of oxidation and break-down processes take place, giving rise to the products mentioned above (trinitrobenzoic acid, trinitrobenzene, tetranitromethane). A decomposition reaction (p. 76) also gives off a large volume of carbon monoxide, which may form an explosive mixture with air. Several explosions of such mixtures have been described.

When nitration is completed, stirring is stopped. TNT separates from the spent acid, forming the upper layer (sp. gr. of TNT at 80°C is 1.467, and at 100° it is 1.443).

Spent acid from trinitration has the composition:

HNO_3	1.5%
H_2SO_4	92.0%
H_2O	4.0%
NO_2	2.5%

Separation of the molten product by decantation at this moment would result in heavy losses, as the solubility of TNT in hot acid is rather high (3.5% at 50%). For this reason the separation of TNT may be carried out in one of the following ways:

1. The reaction mixture is run into a cooling crystallizer. TNT solidifies on the surface of the liquid, forming a crust which is stripped off and washed with water. To the remaining acid 7% water is added, thus changing the solubility of TNT in the acid and causing a second batch of TNT to rise to the surface.

2. Another method of TNT separation from spent acid consists in bringing the TNT to crystallization point by stirring and adding water to the nitrator contents until cool. The reaction mixture is then transferred to filters to separate the crystals from the acid.

From 100 kg of DNT 102 kg of TNT are obtained (theoretical yield 124 kg), which makes about 82% of the theoretical yield.

When calculated on toluene, 190 kg of TNT are obtained from 100 kg (instead of 246 kg calculated theoretically) which makes the actual yield nearly 77% of theory.

Acid usage control. The French method is based on the use of the spent acid from trinitration for dinitration after it has been fortified, and on further utilization of the spent acid from dinitration in the mononitration stage. The composition of the mixtures is calculated as described above.

The spent acid obtained from mononitration by the method described should contain traces of nitric acid (0.2-0.4% of HNO_3). Its absence may be an indication that the amount of nitric acid used for the nitration was insufficient and consequently that part of the toluene has remained unnitrated. In such cases the portion of acid used for the next batches should be richer in HNO_3, since in the old French method the unreacted toluene is not distilled off from the mononitrotoluenes.

The H_2SO_4, content in the spent acid should not be less than 70%. A lower content is not advisable, for a less concentrated sulphuric acid may attack the iron equipment.

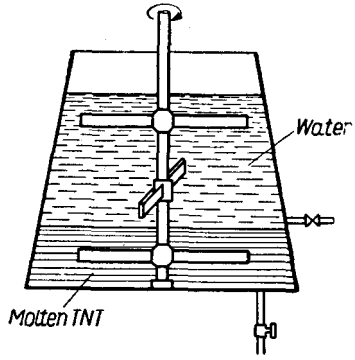


FIG. 78. Wooden tank for washing TNT (Pascal [51].

Washing the TNT and preparing it for final purification. Crude, separated TNT, as described above, is transferred to a separator - a heated iron vessel, in which a temperature of 80°C or somewhat higher is maintained for about 3 hr in order to keep the product therein in a molten state. The remaining spent acid flows down to be then drawn off and added to the main portion of the spent acid. The molten TNT is transferred to a tank in which a preliminary washing (deacidification) is effected. For this purpose wooden tanks, shaped like truncated cones. are used. They are of about 20 m^3 capacity and are equipped with stirrers (Fig. 78).

15 m^3 of water heated to 85°C are run into the tank where this temperature

is maintained by introducing live steam. 4000 kg of molten TNT (the amount obtained from 4 nitrators) are run into the tank and stirred for half an hour. Then the stirrer is stopped and water decanted off. This operation is repeated 3-4 times, then the molten TNT is drained off at the bottom of the tank into pans (2 m x 0.6 x x 0.12 m), six of which are placed on top of each other on carts (Fig. 79).

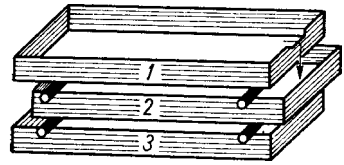


FIG. 79. Pans for crystallization of TNT (Pascal [5]).

The construction of these pans is such as to allow TNT to flow down to the lowest pan after the upper ones have been filled. The TNT solidifies slowly in the and forming large crystals, separated from lower melting impurities, which accumulate in the lowest pan in the form of oil. This product is a grade III TNT ("liquid TNT") used for the manufacture of mining explosives. The main product is removed from the pans, crushed with wooden hammers, and ground finally in a cylindrical mill. During the grinding TNT is sprayed with water to prevent it from emitting dust. The ground TNT is ready for further purification.

OLD BRITISH METHOD [6]

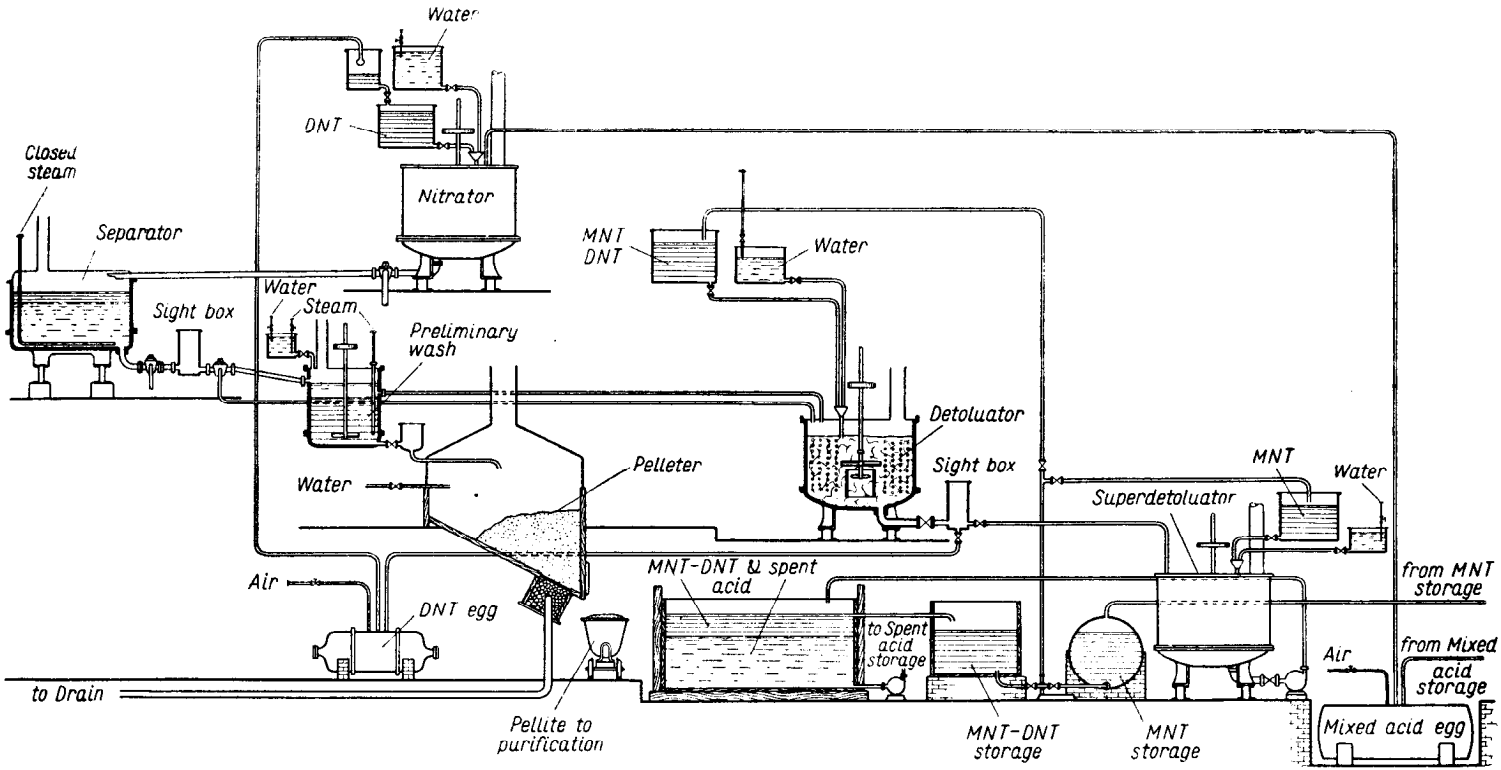
Some features of the British method which was developed during the 1914 1918 period are worth mentioning. One of them was the use of toluene derived from petroleum (Borneo petroleum), as well as toluene from coal.

Petroleum fractions distilling from 95°C to 115°C containing 55-60% of toluene, were used. The remainder constituted aliphatic hydrocarbons which would not nitrate under the conditions of the process. The MNT thus obtained, containing some petroleum components, was purified by distilling off the petroleum fraction.

Detoluation. Another characteristic feature of this method was the extraction of higher nitrated toluene derivatives, dissolved in the spent acids. The latter were conveyed to denitration and distillation (concentration) only after the nitro compounds present in them had been extracted with nitrotoluene, an operation which was called "detoluation". Primarily it consisted in stirring the spent acids, heated to 75-80°C with a quantity of crude MNT, amounting to one quarter of the acid volume. A slight amount of nitrotoluene became nitrated due to the presence of the unreacted HNO_3 in the spent acid.

Later the detoluation operation was combined with partial nitration of MNT to DNT, by adding to the spent acid a certain quantity of nitric acid from the recovery operation (denitration).

Detoluation consisted of two stages, carried out in a detoluator and in a superdetoluator (Fig. 80).



Fro. 80. Diagram of the lay-out of manufacture of TNT with detoluation [6].

The product of trinitration was drained off to a separator, where a temperature of about 80°C was maintained by means of a steam heating coil. When the product had set in two layers the lower one, i.e. the spent acid in a quantity of about 5000 kg, was transferred to the detoluator, into which a mixture of MNT and DNT from a superdetoluator was run with simultaneous cooling and stirring. While maintaining a temperature of 75-80°C by cooling, some 240 kg of 50% nitric acid were introduced into the detoluator and after the mixture had been stirred for half an hour it was cooled to 50°C. About 160 1. of acid water from the preliminary washing of TNT were then added.

Stirring was continued for another 15 min after which the contents were allowed to remain at rest for 30 min in order to set in two separate layers. The batch was then drained off through a sight-glass, the "twice used" acid being directed into the superdetoluator, and the nitro compounds to a pressure-egg, which in turn conveyed them into a tank. From this the nitro compounds were transferred for further trinitration.

Mononitrotoluene along with the acid from which nitro compounds had been partly removed (the "twice used" acid) were run into a superdetoluator, a temperature of 50°C being maintained. Then about 200 1. of water were added to reduce the concentration of H_2SO_4 below 73%. When the mixture had been cooled to 20-25°C stirring was stopped and the nitro compounds were separated and transferred to the detoluator (as described above).

Spent acid of an average composition

H_2SO_4	71.2%
HNO_3	trace
HNO_2	3.0%
organic matter (nitro compounds)	0.4%
H_2O	25.4%

was conveyed to denitration and concentration.

The spent acid from trinitration contained nearly 3.5% of nitro compounds before detoluation.

The composition of the detoluation product was:

30-40% of MNT
40-50% of DNT
20-30% of TNT

It was an oily liquid with a specific gravity of 1.29-1.30.

The extraction of acids with nitrotoluene not only made possible the utilization of the dissolved nitro compounds, but it also enabled direct use to be made of the diluted nitric acid (50% of HNO_3) from the distillation of the spent acid, so that concentration of this acid was not necessary. Apart from the extraction, a partial dinitration took place, the whole process consisting of the following stages:

Toluene -> Mononitration -> Detoluation and preparation of the mixture of MNT, DNT and TNT -> TNT.

Nitration of MNT and DNT to TNT. The mixture of nitrotoluenes was converted into TNT in the following way:

The nitrator was charged with 4800-5000 kg of acids in the following proportion :

H_2SO_4	79.5%
HNO_3	17.8%
H_2O	2.7%

Then crude DNT from the superdetoluator was added at a temperature of 66°C (maintained by heating). The temperature was then raised to 100°C at a rate not higher than 50°C per 10 min. Nitration ended at this temperature and the melting point of a sample of TNT in the nitrator, after it had been acid washed, was 72.5°C (this corresponded to the melting point 76°C of the dry product).

After nitration was completed, 550 1. of water were run into the nitrator to reduce the solubility of the TNT in the acid, and the mixture was then transferred to a separator, where TNT was separated from the spent acid.

After 30-45 mm the acid was drained off through the sight-glass to a detoluator, and the molten TNT to a preliminary washing tank fitted with a mechanical stirrer made of acid resistant material. 160 1. of boiling water were fed into the washing tank prior to the TNT. The mixture was kept boiling by direct steam heating.

Stirring was discontinued after 5 min and after another few minutes the acidic water (containing about 14% of acid) was drained off and transported to the detoluator as described above.

The washed, molten TNT was poured in streams into a granulator, to which a stream of water was also directed, so as to make two streams collide. TNT solidified at once in the form of granules at the bottom of the granulator. Water was run away through a filter, and the TNT, still wet, was unloaded for final purification. The impurities it contained were:

water	about 19.0%
H_2SO_4	0.3%
HNO_3	1.0%
tetranitromethane	0.15%

OLD U.S.S.R. METHOD (ACCORDING TO GORST [7])

The main feature of the old method used in the U.S.S.R. is the presence of separation columns which are combined with each of the three nitrators. Also the spent acid from the third nitration stage is kept for some time in a column in which the nitro compounds swim to the top. The columns are ca. 4 m high and of ca. 2 m diameter. They are made of sheet iron, clad inside with lead.

The flow-sheet is given in Fig. 81. Toluene flows from the tank (1) through the measuring tank (2) to the mononitrator (4). The acid flows through the measuring tank (3). After nitration the products pass through the pressure-egg (5) to the separating column (6). The mono-spent acid flows through (7) to denitration, and the MNT through (8) to the “bubbler” (10) fed through (9) with the spent acid from dinitration.

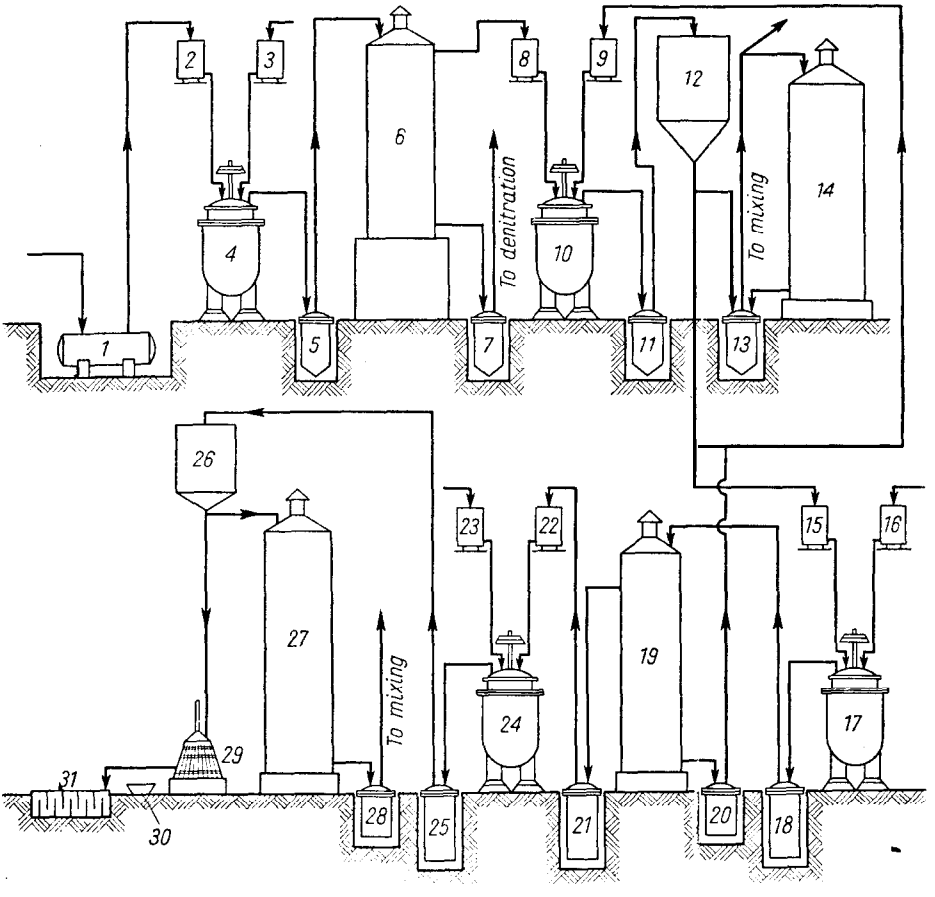


FIG. 81. Flow sheet of the old method of manufacture of TNT in U.S.S.R. (Gorst ([7]).

Here the acid is stirred with MNT to extract dissolved DNT. The mixture from the "bubbler" passes through (11) to the separator (12). The acid freed from DNT enters the separation column (14) and from the column passes to the mixing house to make mononitration acid.

MNT enriched with DNT flows from (12) through (25) to the dinitrator (17) fed with the acid through (16). After nitration the contents pass through (18) to the seperating column (19). The separated acid flows through (20) and (9) to the "bubbler" (10).

The separated DNT flows from the column via the egg (21) and the measuring tank (22) to the trinitrator (24). The nitrating acid flows in from the measuring tank (23). The nitrator contents pass through (25), to the separator (26). TNT from the separator flows to the washing vat (29) and the spent acid to the column (27). Spent acid is sent through the egg (28) to the mixing house. Washed TNT is poured into the pans (39) where it solidifies. The wash water enters the labyrinth (31) and after geos to waste.

The spent acid from the trinitration stage is partly used to make mono- and di-nitration acids, and the rest is diluted to 70-72% H_2SO_4 to separate dissolved

TNT and then sent to denitration. Excess of spent acid from dinitration (14) is diluted to separate dissolved nitro compounds and also sent to denitration.

The main features of the nitration conditions are given below.

TABLE 82

MONONITRATION OF TOLUENE

	Nitration acid	Spent acid
HNO_3	27-28%	0.5%
H_2SO_4	54-55%	68.5%
H_2O	17-19%	18.7-18.8%
N_2O_3	-	1.5%
Nitro compounds		0.7-0.8%
Quantity of the nitrating mixture	103% of theoretical	
Temperature of nitration :		
on mixing reagents	15-40°C	
after „ „	40-50°C	
Time :		
in winter (better cooling)	12-13 hr	
in summer	30-36 hr	
Yield of MNT	95% of theoretical	

TABLE 83

DINITRATION OF MNT

	Nitration acid	Spent acid	
		before "bubbling"	after "bubbling"
HNO_3	23%	2.5%	0.8%
H_2SO_4	67%		
H_2O	10%		
Nitro compounds	-	4%	0.7-0.8%
Quantity of the nitrating mixture	111% of theoretical		
Temperature of nitration :			
on mixing reagents	20-80°C		
after „ „	80-105°C		
Time	8 hr		
Yield	95% of theoretical		

Mononitration of toluene. The nitrator is filled with toluene and nitration acid is added (Table 82).

Dinitration. The nitrator is filled with MNT and nitrating mixture is added (Table 83).

Trinitration. The nitrator is filled with DNT and nitrating mixture is added (Table 84).

TABLE 84
TRINITRATION OF DNT

	Nitration acid
HNO_3	17.5-18.5%
H_2SO_4	81.5-82.5%
H_2O	-
Quantity of nitrating mixture	164% of theoretical
Temperature of nitration :	
on mixing reagents	72-77°C
after „ „	115°C
Time	6-6½ hr

GERMAN METHOD

This method known from the description of the process at the Krümmel. factory was used by the German explosives industry during World War II. Figure 82 represents a flow diagram of the manufacture of TNT by this method.

The characteristic features of the method were:

(1) two-stage mononitration, i.e. a preliminary and a final one;
(2) use of a nitrating mixture prepared from fresh acids for mononitration;
(3) purification of MNT prior to further nitration to DNT;
(4) low temperature during the trinitration process (max. 96°C);
(5) exclusive use of iron in the plant; such units as the washing vessels for TNT being constructed from materials other than wood.

Mononitration. For the nitration of toluene a mixture T_1 of the composition:

HNO_3	28%
H_2SO_4	56%
H_2O	16%

was used.

The nitrating mixture is prepared from fresh concentrated nitric acid, 55% regenerated nitric acid (from the denitration of spent acid), and 96% sulphuric acid recovered by distillation. The mixture of acids is fed into the nitrator from a metering tank through a vacuum started siphon. Toluene is conveyed to the nitrator from another metering tank by means of compressed nitrogen. Air is considered as too dangerous to use, because the explosibility of mixtures of toluene vapour with air.

Plant for mononitration consists of two cast iron pre-nitrators, each having a capacity of 0.5 m3 and a main cast iron nitrator of 15 m^3 capacity. Toluene and acid are run into the pre-nitrators, a toluene to acid ratio of 1 : 2.5 being maintained. The mixture is transferred to the main nitrator through an overflow in the quantity necessary to fill the nitrator (10-12 m^3). A temperature of 34-40°C is maintained in both nitrators by means of a cooling coil.

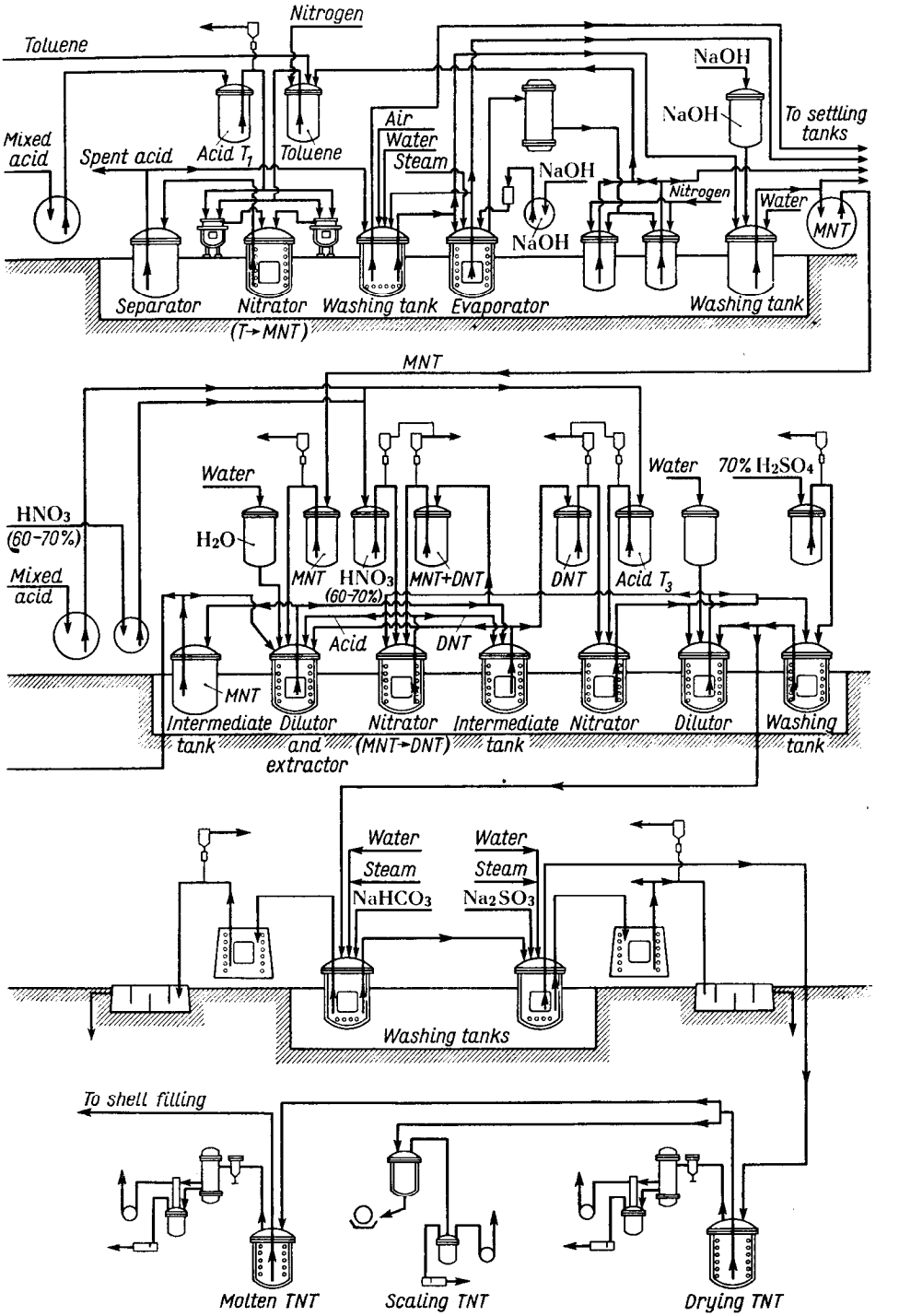


FIG. 82. Flow sheet of TNT manufacture in Krümmel.

The aim of dividing the operation into two stages is to achieve the most effective thermal control, since the conversion of toluene to mononitrotoluene is the most exothermic of all the stages of the reaction, as already mentioned in the section dealing with the theory of nitration. The operation is effected in 5-6 hr. 5000 kg of MNT is obtained from each charge of the nitrator.

When nitration has been completed the reaction mixture is transferred by compressed air to a cast iron separator with a capacity of 15 m^3, where it is allowed to remain at rest for 6 hr to separate into two liquid phases. Then the spent acid is conveyed to a special cast iron tank, where it stays for a few days to recover the temainder of the MNT, which is collected from the surface and added to the toluene to be mononitrated. The spent acid, having a composition:

H_2SO_4	70.0%
NO_2	0.5%
H_2O	29.5%

is conveyed to denitration, which yields 67-68% sulphuric acid. Subsequently this is concentrated by distillation to obtain a 96% product.

MNT thus prepared is washed with water in a wrought iron tank, lined with sheet lead. Washing is effected by vigorous stirring until the product is free from acid (test with Congo red paper). The neutralized MNT is transferred to a so-called distillation unit (of cast iron), where it is mixed with a dilute solution of NaOH, (ca. 1%), the latter being used in a quantity equal to 1 wt. % of MNT (i.e. about 50 kg of NaOH). Washing with alkali not only aims at a complete removal of acids, but also it converts nitrocresols impurities into water soluble nitrocresolates.

Live steam is passed through the mixture of MNT and alkali. The unnitrated toluene and benzene (the latter is a common impurity of toluene) are thus expelled. The steam is introduced until MNT begins to distil, after all the hydrocarbons or other volatile impurities have been expelled. The condensate, containing toluene and MNT, is either recycled for nitration to liquid nitro compounds, e.g. for mining explosives, or is used as a solvent for varnishes.

The alkali layer is separated by decantation and distilled. The MNT recovered is added to the main product. The latter is conveyed from the distiller to a washing tank where it is washed with water, then again with alkali and finally with a sodium carbonate solution. The moist MNT is conveyed by means of compressed air to a cast iron tank for temporary storage.

From 100 parts of toluene 140-144 parts of MNT are obtained by this method, containing about 4% of *m*- nitrotoluene.

Dinitration. Dinitration is carried out in two stages. The first consists of the following operations. The spent acid from trinitration, of the composition:

HNO_3	4-5%
NO_2	34%
H_2SO_4	80%
H_2O	11-13%

having a temperature of about 85°C is fed into a cast iron nitrator of 15 m^3 capacity and cooled to 30°C.

The MNT which has already been used for the extraction of the spent acid from dinitration and which contains some DNT, is introduced at first slowly and then as HNO_3 is used up in the nitration to DNT, the flow rate is gradually increased. The temperature in the nitrator rises to 60-65°C and then falls as the nitric acid is consumed. When all the MNT has been run in, the temperature falls to 55°C. Then the second stage begins. Nitric acid of a concentration of 60-70% of HNO_3 is added. The rest of the MNT is nitrated to DNT, the temperature rising to 70-72°C. The nitration is considered complete when MNT no longer steam-distils from a sample taken from the nitrator.

The reaction mixture is allowed to remain at rest for one hour, then the acid and DNT are separated. The composition of the spent acid is:

HNO_3	0.6%
NO_2	5-6%
H_2SO_4	78-80%
H_2O	13.4-16.4%

The spent acid is transferred to a cast iron dilutor-extractor, and the acid containing DNT goes to a cast iron tank for temporary storage.

The spent acid in the dilutor-extractor is diluted with water to reclaim the greater part of the dissolved DNT. The following composition of the spent acid is obtained on dilution :

HNO_3	0.5%
NO_2	4-5%
H_2SO_4	73%
H_2O	21.5-22.5%

The reclaimed DNT is added to the main yield of DNT, and the spent acid in the extractor is stirred with MNT. Thus the rest of HNO_3 is used for nitration to DNT, and at the same time the dissolved DNT is extracted. The MNT obtained, containing dinitrotoluene, is used later for dinitration.

Spent acid from the extraction process has the following composition:

NO_2	44.5%
H_2SO_4	73-74%
nitro compounds	0.2-0.3%

It is transferred to an intermediate storage tank, where it remains for 4-5 days. During this time the rest of the MNT rises to the surface. It is collected and added to the main portion, while the spent acid is conveyed to distillation.

Trinitration. This can be effected either by adding acid to dinitrotoluene or by the reverse operation.

The acid liquid DNT is metered and fed into a cast iron nitrator of 12 m^3 capacity by means of compressed air. Then acid T_3 of the composition:

HNO_3	24%
H_2SO_4	70%
SO_3	6%

is added. This T_3 mixture is prepared from concentrated nitric acid and 27% oleum. Alternatively, the nitrator may be fed first with acid and then with DNT.

The DNT to acid ratio is 1:2.5-2.6 4000 kg of TNT are obtained per batch, The reaction is completed in 35 hr, and the post-reaction period is 24 hr.

If acid is added to the DNT in the nitrator, the temperature within is kept at 83-85°C, and then raised to 96°C while if DNT is added to the acid, a temperature of 74-78°C should be maintained. When the two substances have been mixed, the temperature is gradually raised to reach 96°C in one hour.

The whole process lasts for 6 hr. Then the reaction mixture is allowed to remain at rest for half an hour, to separate the product from the acid. After separation, the molten TNT is conveyed by means of compressed air to a cast iron washing tank of 8 m^3 capacity and the spent acid to a wrought iron diluter of 15 m^3 capacity.

The TNT in the washing tank is stirred, while hot, with nearly 70% sulphuric acid, to wash out nitrogen oxides and the rest of the HNO_3 or nitrosyl-sulphuric acid. Then it is separated from the acid and transferred to a separate, building for final washing. TNT, after it has been washed with sulphuric acid, contains l-2% of HNO_3 and l-2% of H_2SO_4.

The spent acid, to which the acid from TNT washing has been added, is diluted with sufficient water to obtain the composition given above. The dilution results in further separation of TNT, which is added to the main portion. The diluted spent acid is conveyed to dinitration.

Nitration plant. The nitrators for mononitration (both the pre-nitrators of 0.5 m^3 capacity and the main nitrators of 15 m^3 capacity) are made of cast iron. The same material is used for all other parts of the plant in which not too concentrated acids are processed, e.g. dilutors, washing tank, tanks for nitro compounds, etc.

Those parts of the plant which are used for operations with concentrated acids (e.g. nitrators of 15 m^3 capacity for di- and tri-nitration) arc made of wrought iron.

Washing tanks for the final washing of nitro compounds with water (the water from the operation is slightly acid) are made either from stainless steel or from wrought iron lead lined or they may be constructed of bricks bonded by an acid resistant cement and lined with sheet lead and with acid resistant tiles (Fig. 83).

All pipes for conveying molten TNT from one part of the plant to another are heated either by hot water or steam jackets.

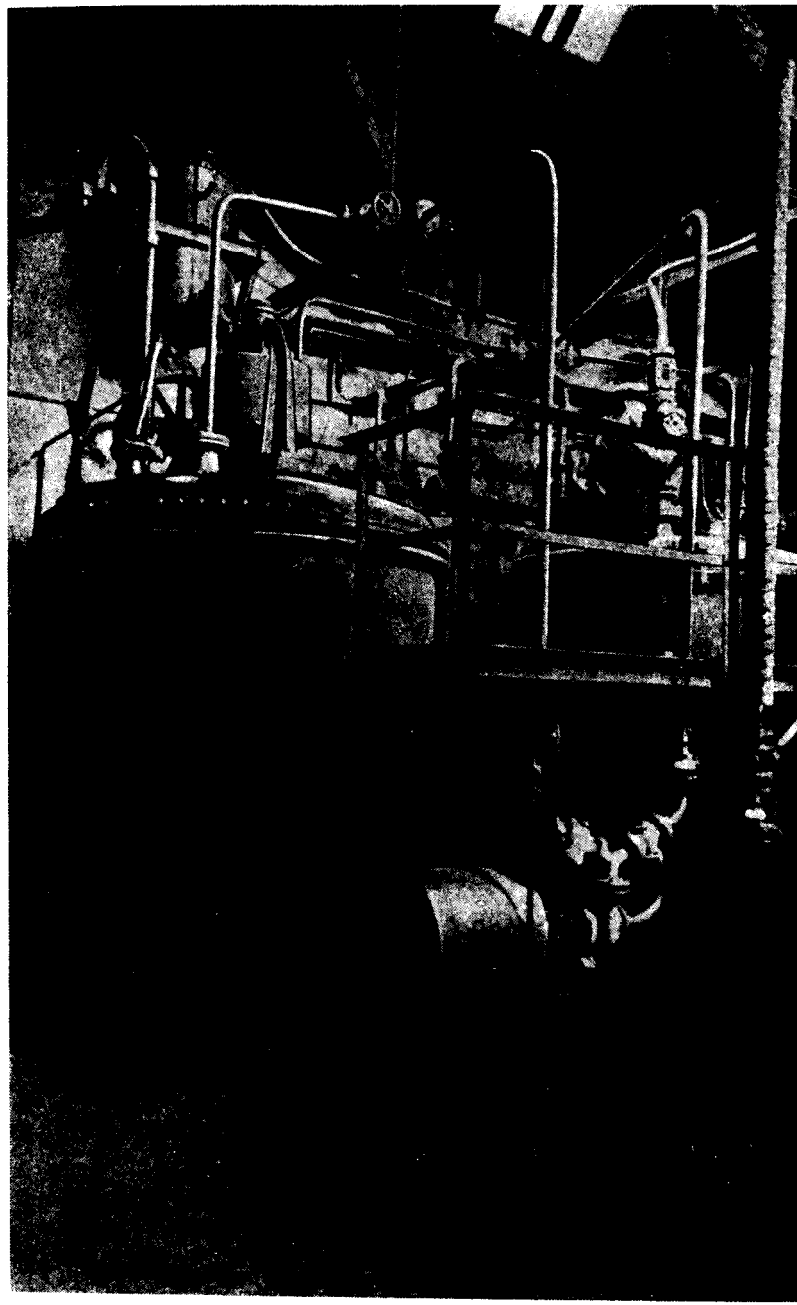


FIG. 83. Washing tank for TNT (Bofors Nobelkrut).

TWO-STAGE MANUFACTURE OF TNT (OLD ITALIAN METHOD)

In Italy a two-stage process of nitration has been used:

Toluene -> Dinitrotoluene -> Trinitrotoluene

For the nitration of toluene to dinitrotoluene a nitrating mixture of the composition :

HNO_3	28%
H_2SO_4	60%
H_2O	12%

is used.

Crude DNT, after it had been separated from acid and washed with water, was sometimes purified by sulphitation. This material partly freed from isomers and derivatives of m-nitrotoluene, was further nitrated.

The trinitration did not differ much from that described above. The mode of separating crystalline TNT from acid is worth mentioning. In this method the nitrator played the role of a crystallizer after nitration had been completed. The reaction mixture was cooled with continuous stirring until crystallization of the TNT began. To initiate the crystallization some water was added to the nitrator. Some of the crystalline TNT obtained in a previous batch might also be added if necessary.

TNT formed crystals which, while still in a hot state, were separated from the spent acid in a vacuum filter or in a centrifuge. The degree of TNT purity could be regulated by temperature during crystallization. A very pure product could be obtained, by using a relatively high temperature (e. g. 75°C).

From the spent acid TNT of lower quality was obtained on cooling. By using a lower temperature of crystallization in the nitrator, crystals of grade II TNT were obtained which in turn could be purified by sulphitation.

Belenkii [8] describes the U.S.S.R. process of crystallization of TNT in the nitrator as follows. TNT crystallization begins at 76°C. This temperature rises by 0.5°C owing to heat of crystallization. By this time the quantity of TNT dissolved in the spent acid amounts to about three quarters of the total. At the initial stage of crystallization, at a temperature of 76°C to 75°C cooling should be very slight. Usually the flow of cooling water to the coil is stopped.

As soon as the temperature falls to 75°C the nitrator contents should be cooled vigorously and simultaneously the speed of rotation of the stirrer should be reduced to avoid pulverizing the crystals. When the temperature has fallen to 30-35°C cooling is discontinued, and almost pure α– trinitrotoluene is filtered off. If the Process of crystallization is properly carried out most of the impurities will remain in the acid.

The TNT is filtered off in a vacuum tank and washed, first with 70% and then with 45% sulphuric acid, each used in the proportion of 800 kg for 1000 kg of TNT, and finally several times with water. By using acid of a gradually reduced concentration for washing a very effective removal of oily impurities of DNT and of isomers of trinitrotoluene can be achieved.

The water-washed TNT contains 0.3-0.5% of acid. This value falls to 0.005% after repeated washing with boiling water.

Pure TNT may be granulated. For this a stream of molten TNT is introduced into a vat, at a place where two jets of cold water impinge on each other (Fig. 84). In this way a product melting at 79.5-80.2°C can be obtained.

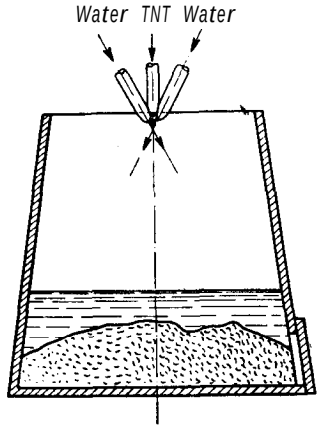


FIG. 84. Granulation of TNT.

The purity of the TNT obtained depends to a great extent on the size of the crystals formed. The best results are achieved when the crystals are of equal size and l-2 mm in diameter.

If grade I crystalline TNT is required the acid free TNT is sulphitated. In this way the melting point may be raised to 80.5°C.

MATERIAL BALANCE

Belenkii [8] reported data on the weight of acids used for 1000 kg of crude TNT (Table 85).

TABLE 8.5

QUANTITY OF ACIDS USED FOR 1000 KG OF CRUDE TNT

Process	Mixed acid (87.3% of HNO_3 and 8.4% of H_2SO_4)		Oleum (104% H_2SO_4) kg	93% sulphuric acid (as H_2SO_4) kg	Spent acid from trinitration kg
	H_2SO_4 kg	HNO_3 kg			
Mononitration	34.4	342.0	-		664.5
Dinitration	35.0	349.0	197.6		841.0
Trinitration	52.2	518.3	1990.0	178.0	
Total	121.6	1209.3	2187.6	178.0	1505.5

The following nitric acid balance for the nitration of over 800 tons of toluene is given below (according to British data of 1914-1918). The balance takes into account both the quantity of nitric acid introduced into TNT in the form of nitro groups and that lost in various ways:

nitric acid used for the formation of NO_2 groups	79.64%
oxidation losses in the form of "fumes" and in wash waters from trinitration	11.22%
losses in mononitration ("fumes", washing out with water)	1.08%
losses at denitration	1.75%
losses in the nitric acid plants	6.31%
Total	100.00%

CONTINUOUS METHODS OF NITRATION

EARLIER METHODS

Although various descriptions of the continuous nitration of aromatic hydrocarbons have been known for a long time (e.g. patents granted to the companies: Meister, Lucius and Brüning in Höchst [9]; Weiler-ter-Meer in Uerdingen [10]; Westphalisch-Anhaltische Sprengstoffe A. G. [11] and a well-known patent granted to Kubierschky [12]), until recently these methods were not widely used. Particularly in the explosives industry, conservatism and fear of the adoption of any new untraditional methods not known to be safe, have been strong enough to prevent their realization. Hence most of the proposed methods have not been put into practice.

Methods of continuous nitration of aromatic hydrocarbons may be based on one of the following principles:

1. *Nitration in the vapour phase.* In methods of this kind (e.g. the Wilhelm method [13]) a continuous stream of vapours of the aromatic hydrocarbon and nitric acid or nitrogen dioxide is introduced into the reactor. Sulphuric acid is not used in this reaction.

One drawback of this method common to all processes taking place in the gaseous phase, is the necessity of using very large units, much larger than the capacity of the reactors for liquid processes. These methods have not found any practical uses.

2. *Partial pressures method.* Othmer and his co-workers [14-16] have suggested amethod in which a mixture of hydrocarbon and nitric acid of about 61% concentration is boiled. The water liberated in the reaction is distilled off with part of hydrocarbon, as an azeotrope. The two components are separated in a receiver into two layers, the water being drained off and the hydrocarbon recycled. As a result of the reaction mono- and di-nitro derivatives can be obtained. The method has been developed on the laboratory scale only.

3. Counter-current method. The method was suggested by Kubierschky [12]. The nitrator for nitrating benzene to nitrobenzene takes the form of a column. A mixture of nitric and sulphuric acids is introduced at the top while a mist of hydrocarbon is fed in at the bottom. The middle part of the column plays the role

of nitrator. The nitration product collects at the top, where it flows off continuously, while the spent acid, which concentrates at the bottom, always flows downwards.

There is no need for a stirrer as the reacting liquids are mixed by the natural flow resulting from the difference in specific gravities of the components. Because of certain drawbacks inherent in the difficulty of removing the heat of reaction, and as an emulsion may be formed, the method has not found any permanent practical uses.

4. *Co-current method.* Such methods are described in patents, granted to Meister, Lucius and Brüning [9] and to Weiler-ter-Meer [10]. The nitrating mixture is fed to the nitrator simultaneously with the hydrocarbon to be nitrated. A set of nitrators arranged in series may be applied to make the nitration more complete.

In industrial practice the co-current and co-current-counter-current methods are used. Thus, for example, the process in single nitrators may be based on a co-current principle while a number of nitrators may be connected in such a way as to work as a battery of counter-current system.

MODERN METHODS

The continuous methods are in many respects superior to the batch methods. One of the advantages of the continuous methods is that a much lower quantity of explosive accumulates at any moment in the plant. According to A. B. Bofors [17], in a plant with a daily production of 7.5 tons of TNT by the batch process, 10 tons of explosive were accumulating at any moment in a volume of plant of ca. 50 m^3. The corresponding figures for a plant with twice the capacity run continuously are 4 tons and 12 m^3 respectively.

With regard to the hazards involved, the modern continuous methods offer a much higher degree of safety, thanks to automatic regulators which keep control over the rate of feed into the nitrators and separators, the temperature of the reaction etc. In the event of a breakdown in the power supply (which usually involves danger due to the stoppage of stirring) all proportioning apparatus automatically stops and the reacting quantities in the nitrators are too small to produce any alarming rise of temperature.

All the reactors are provided with regulators controlling the supply of cooling water so as to keep the temperature constant. The regulators are so connected that in the case of a power interruption, they will fully open the feed of cooling water. Accordingly since no special action is required of the operator, he may simply leave the building when a power failure occurs.

One of the advantages of the modern methods is the small size of the apparatus. According to A. B. Bofors [17], a continuous plant with a daily production of 15 to 40 tons requires a floor surface of only ca. 150 m^2 in a one-storey building.

British method

The detoluation method was developed as a continuous method of manufacturing TNT in the Oldbury plant which came into operation in 1917.

In this plant each of the nitrators is connected with a separator, into which the liquid from the nitrator overflows and where the nitro compound is separated from the acid. The upper, nitro compound layer then flows to the next nitrator, containing a more concentrated acid, while the lower acid layer passes through a siphon to another nitrator, where less vigorous nitration takes place. Both liquid phases-that of the acid and that of the material being nitrated-flow in counter-current to each other. Figure 85 represents a schematic diagram of a unit for continuous nitration (after MacNab [18]).

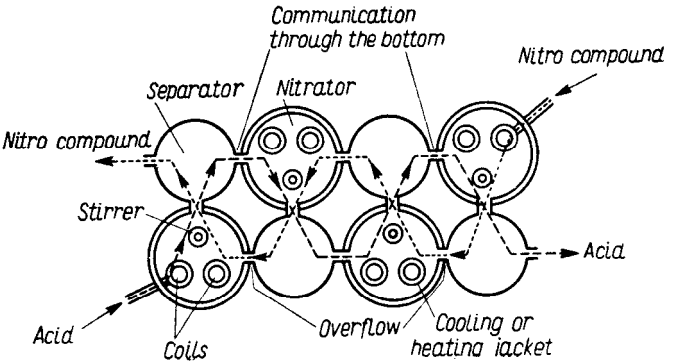


FIG. 85. Diagram of the British continuous nitration of toluene to TNT (according to McNab ([18]).

The unit comprises 14 nitrators and 14 separators. The first nitrator is fedwith nitrotoluene, prepared in another unit by the batch process. Nitrators from (2) to (14) are fed with acids of an increasing concentration. The acid in the "middle" nitrators, from (5) to (22), is of the following composition:

HNO_3	8-10%
NO_2	1%
H_2SO_4	80-82%
H_2O	11%

Into nitrator (24) a nitrating mixture prepared from 96% sulphuric acid and anhydrous nitric acid is introduced. The spent acid flowing from nitrator (2) to nitrator (I) is detoluated here by agitating with nitrotoluene whence it flows away as waste acid of the composition:

HNO_3	1%
NO_2	4%
H_2SO_4	78-80%
H_2O	14-16%
organic matter	1-1.5%

In the nitrators the following temperatures are maintained:

Nitrators	1-2	40°C
	3	70°C
	4-13	100°C
	14	90°C

The composition of the nitration products obtained in the separate nitrators is reflected by the melting points of the products:

Nitrator	3	15°C	Nitrator	9	55°C
	4	35°C		10	63°C
	5	50°C		11	69°C
	6	45°C		12	72°C
	7	41°C		13	76°C
	8	35°C		14	77°C

The formation of trinitrotoluene begins in nitrator 5. For 1000 kg of TNT

470-480 kg of toluene
1090-1160 kg of HNO_3
410-440 kg of H_2SO_4

are used in the process.

German method

During World War II a continuous process for nitrating toluene to TNT developed by J. Meissner [19] and patented in 1941 was introduced at the Schlebusch factory in Germany. The nitration unit consisted of 5 nitrators and 4 separators, as shown in the schematic diagram in Fig. 86. Both the nitrators and the separators

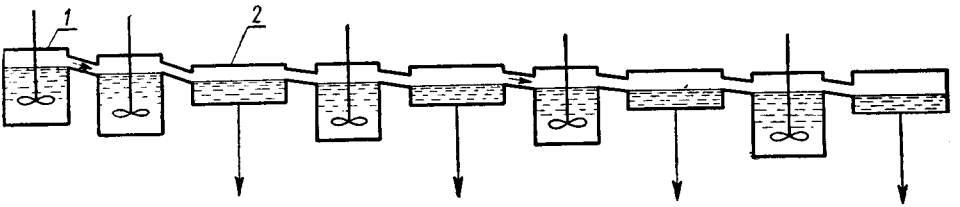


FIG. 86. Diagram of the German continuous nitration of toluene to TNT (CIOS XXIV 4).

are arranged in a cascade so as to enable the liquid to flow down from higher vessels to lower ones. In this way the nitration mixture can be transferred from the nitrator to the separator, where the nitro compound rises to the surface and flows off through a drain between the separator to the next nitrator. The waste acid flows down from the bottom of the separators to storage tanks.

The nitrators are 1.5 m high and 1 m in diameter. The separators are 0.75 m high and 1.5 m in diameter. Both are fabricated from cast iron.

Recently F. Meissner, Wannschaff and Othmer [20] have published some data on J. Meissner's continuous method of preparation of TNT, which is an improvement of an earlier patent of Meissner's.

The design of the plant is based on the combination of the co-current process with the counter-current-battery system. The plant consists of three aggregates, each of them comprising the following stainless steel parts:

(1) tanks for reactants and metering tanks for the continuous supply of nitrating mixture and hydrocarbon;

(2) the main nitrator ;
(3) one or more supplementary nitrators;
(4) a vessel for extraction of the waste acid (detoluator);
(5) two separators.

A schematic diagram of such a nitration unit with a washing column and a separator is shown in Fig. 87.

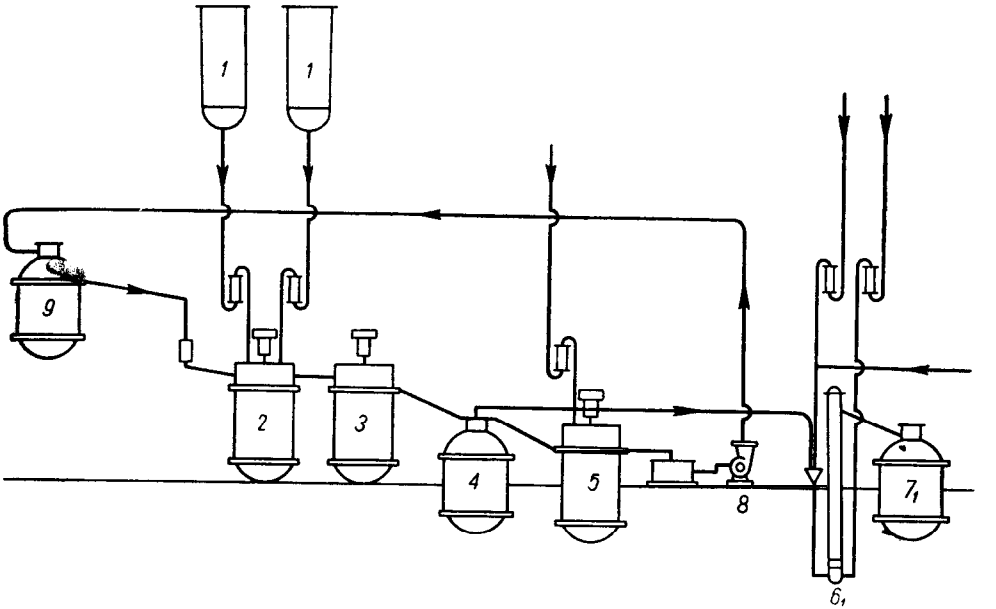


FIG. 87. Flow-sheet of continuous nitration of toluene according to J. Meissner ([20]).

The acid and toluene are introduced from tanks (1) to the nitrator (2), in which the main part of the nitration proceeds. From here the contents pass to another nitrator (3), and if necessary to still another where the reaction is completed. The nitrators are arranged in series, each of them being operated co-currently. The reaction mixture passes from nitrator (3) to separator (d), where the separation of the nitro compound from the waste acid takes place. The nitrotoluene then flows to a system of washing tanks ((6) is the first of these). The waste acid passes to vessel (5), also continuously fed with toluene. By stirring the spent acid with a very small quantity of toluene, the former is freed from any nitro compounds present and at the same time the nitric acid still remaining in the spent acid (1-3%) reacts with toluene to yield nitrotoluene. The purified acid along with toluene is transferred by pump (8) to separator (9), where they are separated. The toluene, still containing some nitrotoluene, is introduced to the main nitrator (2), in a continuous way, thus realizing the counter-current principle and the spent acid, now containing only about 0.3% of HNO_3 and not more than 0.5% of aromatic compounds, goes direct to concentration, previous denitration being unnecessary here.

Nitrators for continuous nitration are of about one twentieth the size of reactors for the batch process. They are equipped with very efficient stirrers and fitted with an external jacket and a coil for conducting away the reaction heat. Rotameters, measuring with an accuracy of about 1%, are used for proportioning the reagents.

The nitrotoluene produced in the first aggregate is sent to the second one, where further nitration to dinitrotoluene takes place in a similar way as that described above. Finally, in the third aggregate, nitration to trinitrotoluene occurs.

For the first nitration stage (toluene to mononitrotoluene) a mixture of 96-98% sulphuric acid and 60% nitric acid is used. Sulphuric acid is taken in such as quantity as to obtain the concentration of about 70% of H_2SO_4 in the acid after the first stage of nitration.

The loss of sulphuric acid is about 1% of the quantity used. A 1.5% excess of acid is used over the required amount theoretically. The yield of nitrotoluene is 98% of theory.

The quantity of alkali required for the neutralization of the wash water does not exceed 0.5% of the weight of nitrotoluene.

The unit is easy to operate. It is claimed that at an output of 20-60 tons of TNT a day (larger units are not advisable) not more than one skilled worker is needed.

The separation of the production unit of mononitrotoluene from the next stages of nitration is desirable so as to provide the mononitration unit with a unit for removing m-nitrotoluene by distillation. A mixture of *o*- and *p*- nitrotoluene or *o*- nitrotoluene alone is then used for further nitration. In the latter case *p*- nitrotoluene is utilized for the preparation of dyes (from *p*- toluidine, derivatives of stilbene, etc.) and pharmaceuticals (*p*- aminobenzoic acid.)

Swedish Bofors-Norell method

The Bofors-Norell process [21] was tried out in 1940-41 and has now been in full-scale operation for nearly two decades. The process includes both continuous nitration of toluene or mononitrotoluene to trinitrotoluene and continuous crystallization of the product from dilute nitric acid.

The nitration is carried out continuously in a series of nitrators through which the nitrating acids and toluene or nitrotoluenes pass in counter-current. Each nitrator is joined with a separator.

According to A. B. Bofors both nitrator and separator have been designed in such a way that no pumps or conveyors are needed to transport the nitrating acid and the nitrated product between the different nitrators. Reactants are supplied continuously in quantities adjusted by means of proportioners. The continuous flow of waste acid from the mononitration stage and also of trinitrotoluene keeps the plant running constantly.

One of the features of the method is its lower temperature as compared with the former Bofors discontinuous method which required a temperature up to 140°C at the last stage of nitration.

All nitrators are provided with regulators controlling the supply of cooling water. According to A. B. Bofors, the raw material consumption per 1000 kg TNT is as follows:

toluene	450 kg
nitric acid (99%)	1000 kg
sulphuric acid (100%) supplied in the form of 95% sulphuric acid and oleum	1850 kg

A flow sheet and general view of the Bofors plant is given in Fig. 88 and 89 respectively. A general lay-out is given below (Fig. 101).

Swedish-Norwegian Chematur and Norsk Spraengstoffindustri method

This method [22] patented in Sweden in 1953 employs stepwise nitration of mono- and/or di-nitrotoluene to trinitrotoluene in a series of counter-current units, each unit consisting of a nitrator and a separator.

The principle of the design of the unit is given in Fig. 90. Nitrator N consists of a U-vessel with two legs or shanks (1) and (2) joined by pipe (6). The components of the reaction are introduced through inlets (4) and (5). Liquid can be kept in circulation from leg (1) to leg (2) and back by the turbine-wheel (8) on the driving-shaft (7). By regulating the speed of the turbine (8) and adopting suitable proportions for pipes (3) and (6) it is possible to keep the liquid at a higher level in leg (2) than in leg (1). Separator S communicates with the nitrator through pipe (9). The separator is shaped as a rectangular box (10) with distributor (II) for the mixture coming from the reactor, an outlet (12) for the separated light component and an outlet (13) for the heavy component. At some distance from the inlet and between the levels of the outlets for the separated components there is also another outlet (14) for partly separated emulsion. This outlet has adjustable plates (15) and (16) to make it possible to adjust the opening of the outlet with reference to its level in the separator. The partly separated emulsion is led back to the reactor through pipe (18) and regulating valve (17). To control the temperature of the reaction mixture the unit is equipped with heat exchangers (19) and (20). The separator may also have a heat exchanger jacket not shown in the diagram.

The unit is operated in the following way. The reactants are introduced through inlets (4) and (5), mixed with the help of turbine (8) and circulated through pipe system (1), (3) and (6) chemical reaction and physical exchange being simultaneously effected. They are continuously transported to the separator in the form of an emulsion. In the separator the components are separated, the light component (nitro compounds) rising to the surface and flowing off continuously through outlet (12). The heavier component (spent acid) sinks to the bottom and is removed continuously through outlet (13). In the area between the separated components the partly separated emulsion is withdrawn and led to mixing part of the reactor. This transport is possible because the level of the liquid in the separator through leg (2) is higher

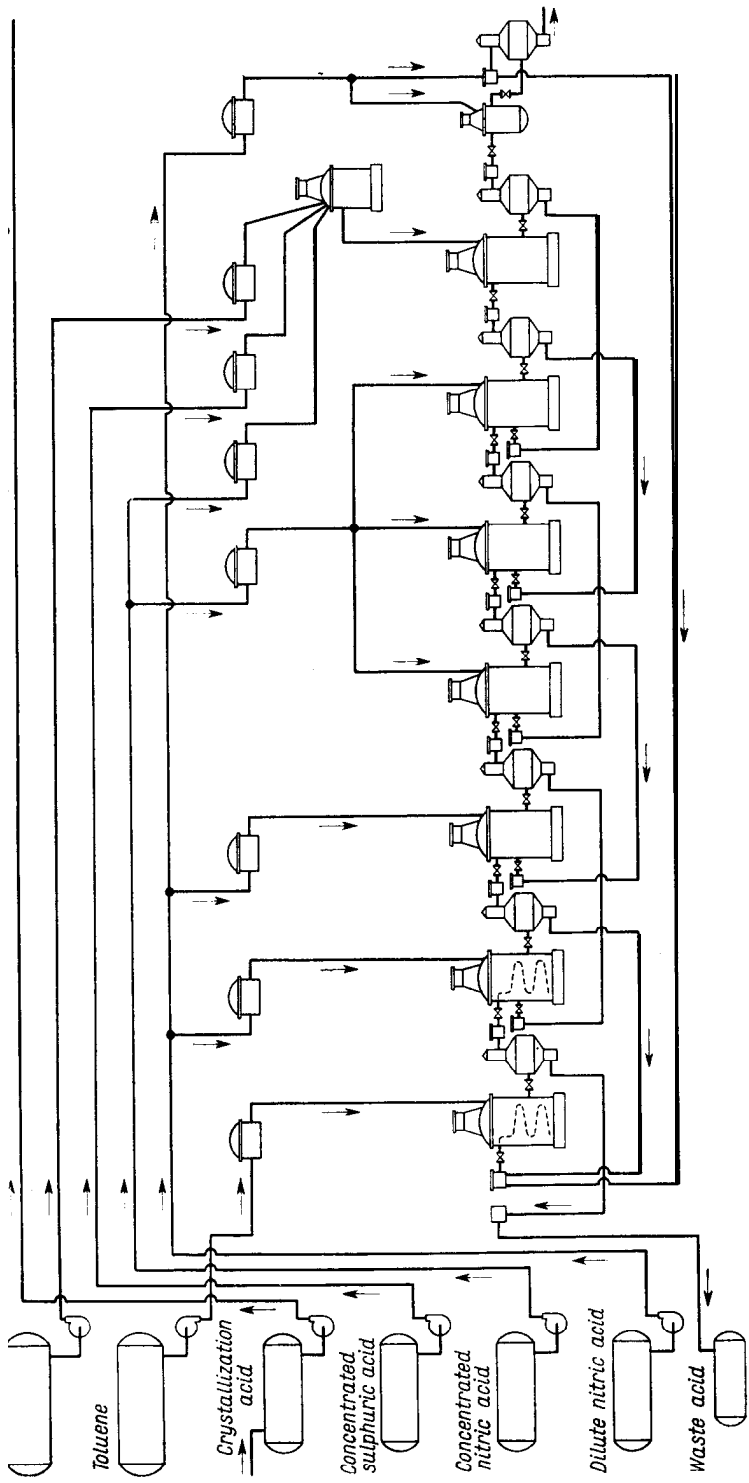


FIG. 88. Flow-sheet of Bofors-Nobel method of continuous manufacture of TNT ([17]).

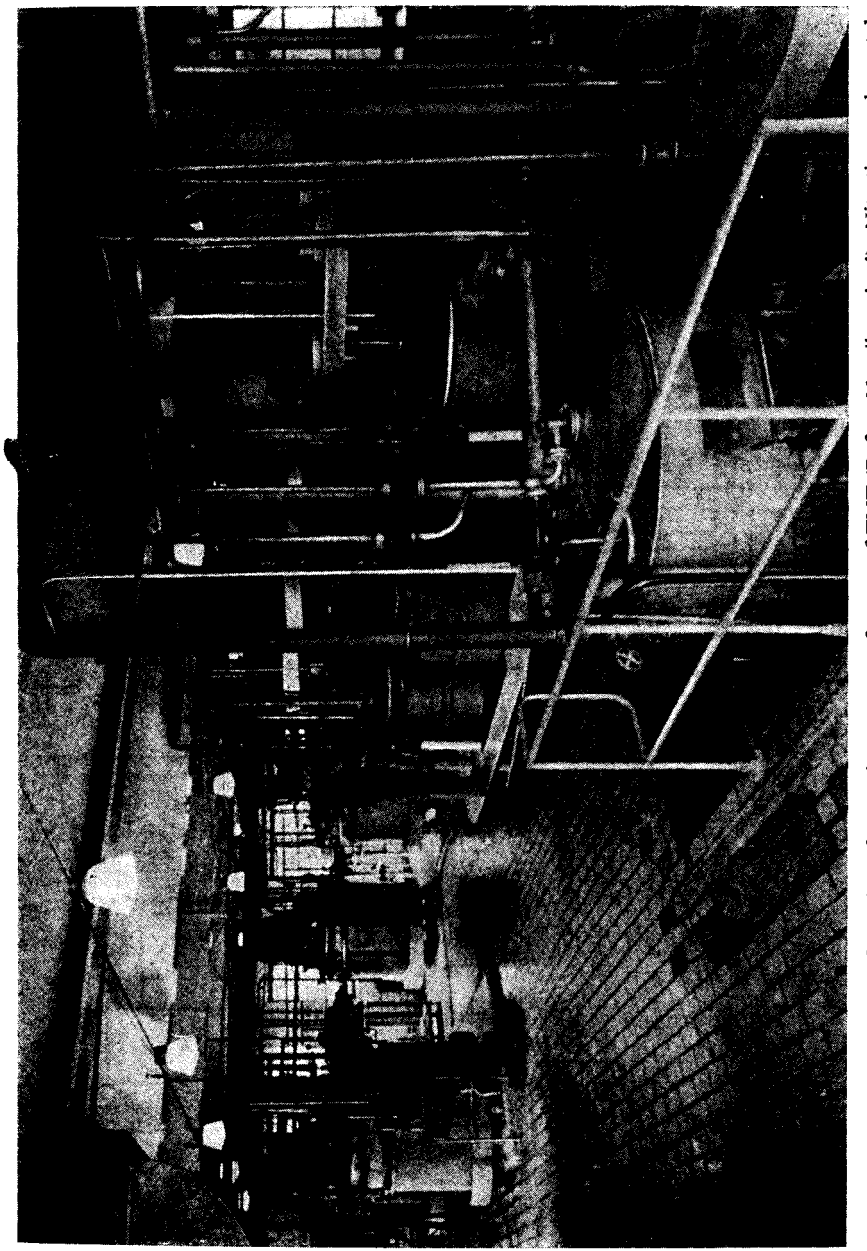


FIG. 89. General view of Bofors plant for continuous manufacture of TNT (Bofors-Norell method). Nitration and crystallization of TNT.

than in leg (1). The rate of feed of partly separated emulsion can be regulated by means of valve (17).

With plates (15) and (16) adjusted to lower levels of the fedback currents through

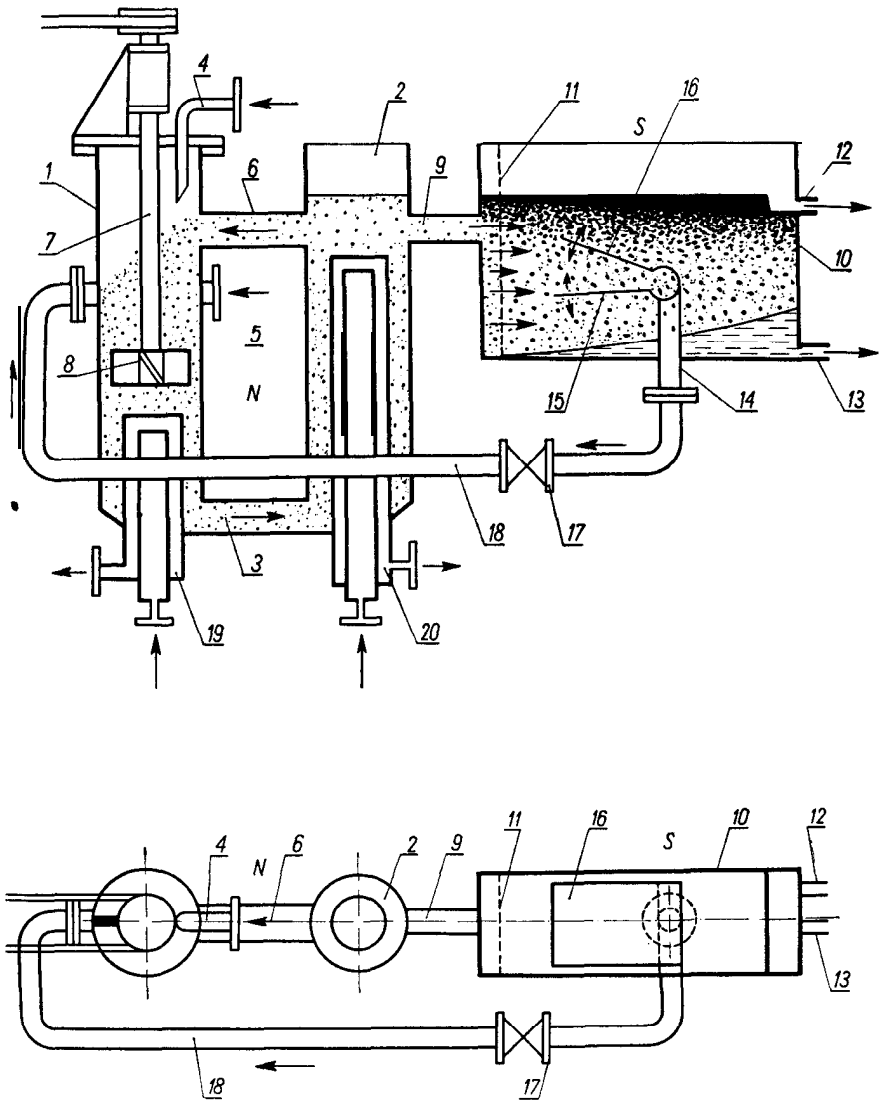


FIG. 90. Nitrator for continuous manufacture of TNT (Chematur method ([22]).

pipe (18) they will be more enriched with the heavy component and this component will therefore be concentrated in the system.

If eighteen nitrating units are applied, the composition of the nitrating mixtures and the temperature during the process will be as follows (Table 86).

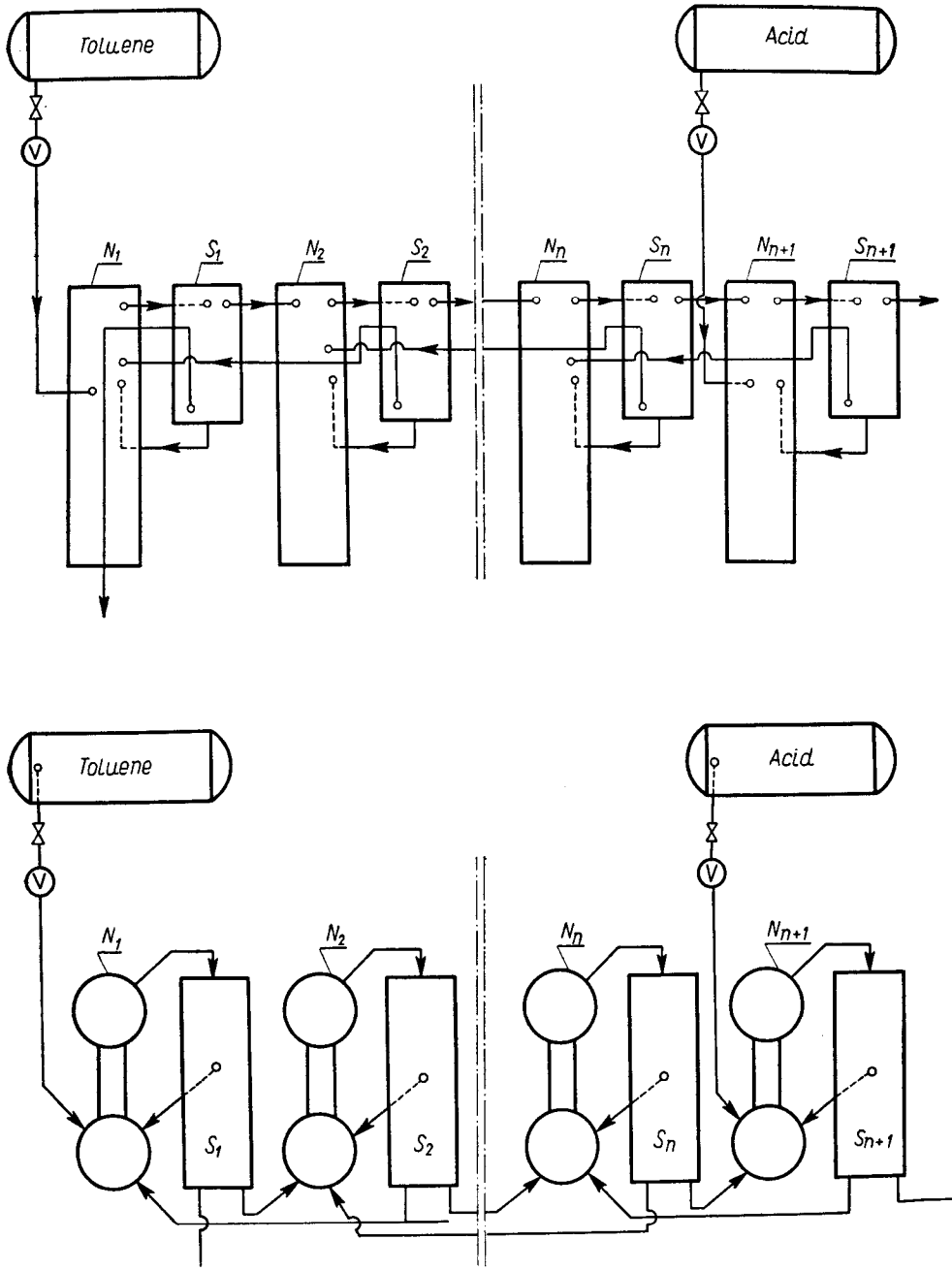


FIG. 91. Diagram of a system of nitrators (N) and separators (S) in the Chematur method of continuous manufacture of TNT [22].

The yield of TNT is as high as 97-99% of theory.

If an unfractionated mixture of the mononitrotoluene isomers is used (i.e. the product of straight nitration of toluene), TNT with a melting point of 78.7°C results. If the starting material is free from *m*- nitrotoluene, e.g. if pure *o*- nitrotoluene is used, TNT with a melting point of 80.6°C is produced.

TABLE 86

Nitrators Nos.	Composition of nitrating mixtures, %			Temperature °C
	HNO_3	H_2SO_4	H_2O	
1-3	0.9	89.2	9.9	65
4-6	3.0	90.1	6.9	75
7-9	7.9	87.8	4.3	80
10-12	7.5	89.8	2.7	85
13-15	7.5	91.4	1.1	90
16-18	7.7	91.8	0.5	90

PURIFICATION OF TNT

In the purification of TNT the following impurities have to be removed:

(1) traces of nitric and sulphuric acids;

(2) unsymmetrical isomers;

(3) products of incomplete nitration;

(4) by-products (tetranitromethane, trinitrobenzene, nitrobenzoic acids, nitrocresols, etc.).

The aim of final purification is to remove all those products which are present TNT and which are more reactive than TNT itself (isomers, nitrocresols, nitrobenzoic acids etc.) or which can easily give oily exudation products (isomers, lower nitrated substances).

The oily exudation product (TNT-oil) is very undesirable for the following reasons :

(a) Exudation produces porosity of the TNT charge and reduces its density. This reduces its explosive effect. In artillery shells it can produce a dislocation of the charge on firing, compression of the air included in the cavities, and premature explosion.

(b) The oily products can penetrate into the threaded parts of the shell and form “fire channels” through which the ignition of propellant can ignite the charge.

(c) The oily products can penetrate into the detonating gaine if the charge of the gaine is unprotected by a metal envelope (e.g. former English gaines made up of TNT in a silk bag). The oily products reduce the detonating powers of the gaine.

The first purification step is thorough washing of the TNT with hot water, in washing tanks or by emulsification.

PURIFICATION BY CRYSTALLIZATION

In the past the TNT, washed free from acids, was further purified by crystallization. For this purpose 95% alcohol was mostly used. Since alcohol is not a very good solvent for TNT, in several countries it was customary to add a certain quantity of benzene (e.g. 5%) as in Germany before World War II. In other countries toluene was added. Since benzene and toluene vapours are more toxic than that of alcohol, in some U.S.S.R. factories alcohol alone was used for the crystallization.

Various other solvents for the crystallization of TNT have been suggested: carbon tetrachloride (U.S.A., World War I), benzene, *o*- nitrotoluene (Stettbacher [23]). More modem method consists in crystallizing TNT from nitric acid (see below under continuous method of crystallization).

With the outbreak of World War I the shortage of alcohol compelled German factories to give up the crystallization method and to confine purification either to thorough washing with hot water or to crystallization by dissolving the TNT in concentrated sulphuric acid followed by precipitation with water (Vender's method [24]). The precipitation could be controlled by adding sufficient water to allow lower nitrated and unsymmetrical derivatives of TNT to remain in solution.

After the war the method of purification by crystallization was not resumed, as purification by means of sodium sulphite was introduced.

The reason why the use of alcohol for crystallization was abandoned can be ascribed to the constant risk of fire when handling a large quantity of this volatile and inflammable solvent. Attention had been drawn to this by the explosion which took place in the TNT drying building at the Allendorff factory in Schbnebeck in 1909. The cause of that dangerous explosion which destroyed both the crystallization building and the drying building was fire started by ignition of the mixture of alcohol vapour and air. It is very likely that the fire started in a centrifuge where TNT had been separated from the solvent after crystallization. The crystallization of TNT from alcohol solution had been the cause of many other fires, so when sulphitation was developed it was readily adopted.

Although the purification of TNT by sodium sulphite was widely used after World War I a number of factories continued with the crystallization method using among other solvents toluene, which directly after crystallization was used for nitration.

In the United States a method of purifying TNT by washing with xylene is used (after Clift and Fedoroff [25]). The method is based on the view that the isomers of α– trinitrotoluene are located mainly on the surface of the grains of solid TNT. For purification, TNT is mixed with xylene in the cold, then the latter is filtered Off on a vacuum filter. The operation is repeated with a smaller quantity of xylene the mixture is passed again through a filter and the rest of the xylene is removed by pressing to a content of 3-4%. Finally the product is dried under vacuum, at 60°C. The xylene from the washing operation is sent to distillation.

The residue left after the solvent - alcohol (in the earlier crystallization method) or xylene (from the washing technique) - has been distilled off, is a semi-solid substance consisting of α– trinitrotoluene, its isomers, dinitrotoluenes and other nitro compounds, all of them found as impurities in TNT.

The mixture, known as "TNT oil", generally melts within a wide temperature range, for example from room temperature up to 60°C. It may be used as a component of ammonium nitrate explosives for the mining industry.

The "exudation process" is a modified purification by crystallization. At present it is applied to purify grade III TNT and to recover impurities present in TNT for use as "TNT oil" in the preparation of explosive compositions. The process may be carried out in two ways.

In one of them TNT, scattered over sloped flat pans (Fig. 79, p. 351), is put into a chamber heated to 60°C. After several hours the low-melting impurities segregate as oil which collects in a special vessel placed below the pans.

Another method consists in melting TNT in tilting kettles (converters) heated by steam or hot water which are then left at rest at room temperature or slightly higher (e.g. 30°C) for slow crystallization. Under such conditions large crystals of TNT are formed immersed in an oily mixture of other nitro compounds. The latter is removed by breaking the solidified substance and inclining the kettle so as to enable the oil to run out.

The oily product has been used as an ingredient of coal mining explosives as so-called "liquid TNT". This material also comprised the liquid mixture of nitro compounds forming the residue after distillation of alcohol (or any other solvent) used for crystallization of TNT.

In an earlier Russian method (Belenkii [8]) crude, granulated TNT was washed with hot water in wooden tanks lined with sheet lead, and equipped with an air bubbler.

For a batch of 1000 kg of TNT 1000 l. of water were used at a time. The water was brought to boiling by direct heating with steam (1-2 hr). After boiling for 5 min heating and air mixing were stopped, and the TNT allowed to settle at the bottom. After 10-15 min the water was separated by decantation. This operation was repeated 6-8 times with new portions of fresh water, until the acidity of the TNT fell to 0.02% (calculated on H_2SO_4). The whole washing process took about 7 hr. The use of lead-lined tanks for the first two washings, and a wooden tank for the next ones proved advantageous,

Norell [26] invented a continuous method of crystallization of TNT from nitric acid. A diagram is given in Fig. 92, according to the A. B. Bofors patent.

The crystallizing vats (1).-(5) are provided with heating jackets (3) and stirrer (4). The vats communicate through the overflow (7) and pipes (6). The last crystallizer has an outlet (8) provided with a screw type conveyer to remove a semi-solid mixture of crystals of TNT plus mother liquor.

The first vat is provided with pre-crystallizer (9) and a stirrer (10). The molten TNT (II) and solvent (12) (i.e. nitric acid) is introduced to the pie-crystallizer in which TNT

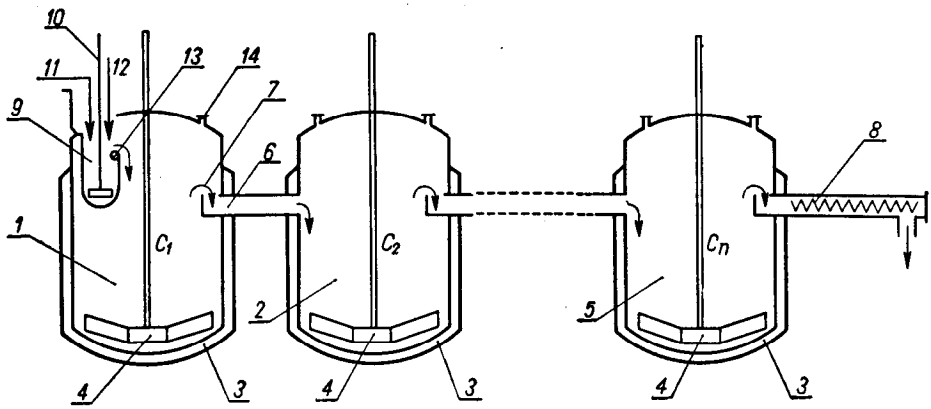


FIG. 92. Continuous crystallization of TNT (Bofors-Norell method [26]).

is dissolved. The solution flows to the crystallizer (1) through an overflow weir (23). Mechanical impurities are held back by the weir. The crystallizer decks are provided with apertures (24). Vat (1) is heated, vat (2) is cooled. Here crystallization begins, and is ended in vat (5).

SULPHITATION AND DRYING OF TNT

There are various methods of purification of the TNT with sodium sulphite.

French method

In the French method the ground TNT is mixed with a 7.5% solution of Na_2SO_3 at room temperature for 2 hr. The operation is carried out in wooden vats, 1.3 m high and 1.3 m in diameter (Fig. 78), using 750 kg of TNT and 750 1. of the solution at a time. Then the mixture in the vat is drained off to a vacuum filter, where the TNT is filtered off, washed with water four times, and sent to a drier.

For drying, an iron vessel of construction similar to that of the nitrator, is charged with TNT (2250 kg). The TNT is melted by passing steam through the jacket of the drying vessel, after which dry air is passed from the bottom through the molten product.

The vessel is covered by a hood with a ventilation pipe through which the moisture escapes (Fig. 93). Initially a temperature of 90°C is maintained, and toward the end of the operation it is raised to 105°C to let the rest of moisture escape.

@he-dry, molten TNT is -subsequently flaked. The equipment for this, operation consists of a rotating steel drum (I), cooled by water from inside. The lower part of the drum is dipped in molten TNT, the temperature of which is about 80°C (Fig. 94). The cooled surface of the drum causes the TNT to solidify on it, and a bronze knife (2) scrapes off the TNT coating in fine flakes, which fall into hopper (3). Flaked TNT is the most convenient form for transport, storage and further use, and is therefore the most widely used form of this substance. Alternatively pure TNT is sometimes used in the form of granules, obtained by granulating in cold

water. For this purpose the installation described on p. 364 may be used, in which a stream of molten TNT ejected under pressure impinges on two streams of cold water at their point of contact (Fig. 84). Grains of TNT together with water fall into a tank, and are conveyed to a centrifuge or to a vacuum filter. To remove water the product is dried in a tunnel or tray drier at 50-60°C, i.e. at a temperature below its melting point.

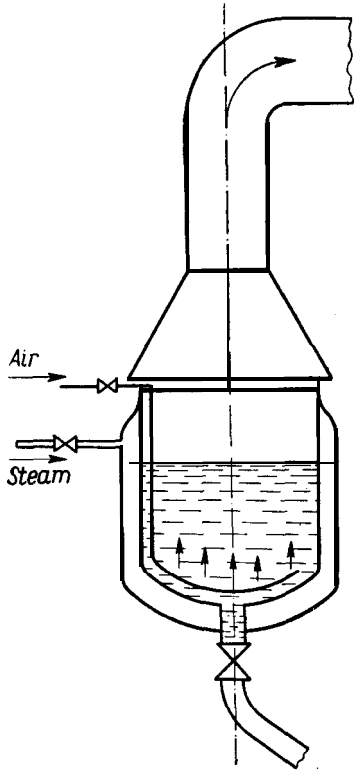


FIG. 93. Vessel for drying TNT.

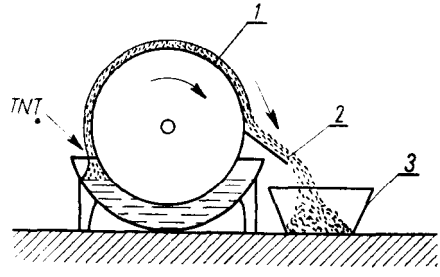


FIG. 94. Flaking of TNT.

The water and liquors from washing and sulphitation of TNT contain some TNT both dissolved and suspended. For recovering the latter the water and wash liquor are conveyed to "labyrinth" tanks equipped with baffles barring the passage of suspended TNT, which settles at the bottom. In this way a certain amount of lower grade TNT may be recovered.

British method

In the British method, crude, granulated TNT prior to sulphitation is washed either batchwise - an operation not differing from the one described above - or continuously.

The plant for continuous washing (Fig. 96) consists of a rectangular trough, 8 m long, 1.4 m wide and 1.3 m high. The trough is made of cast iron sections screwed

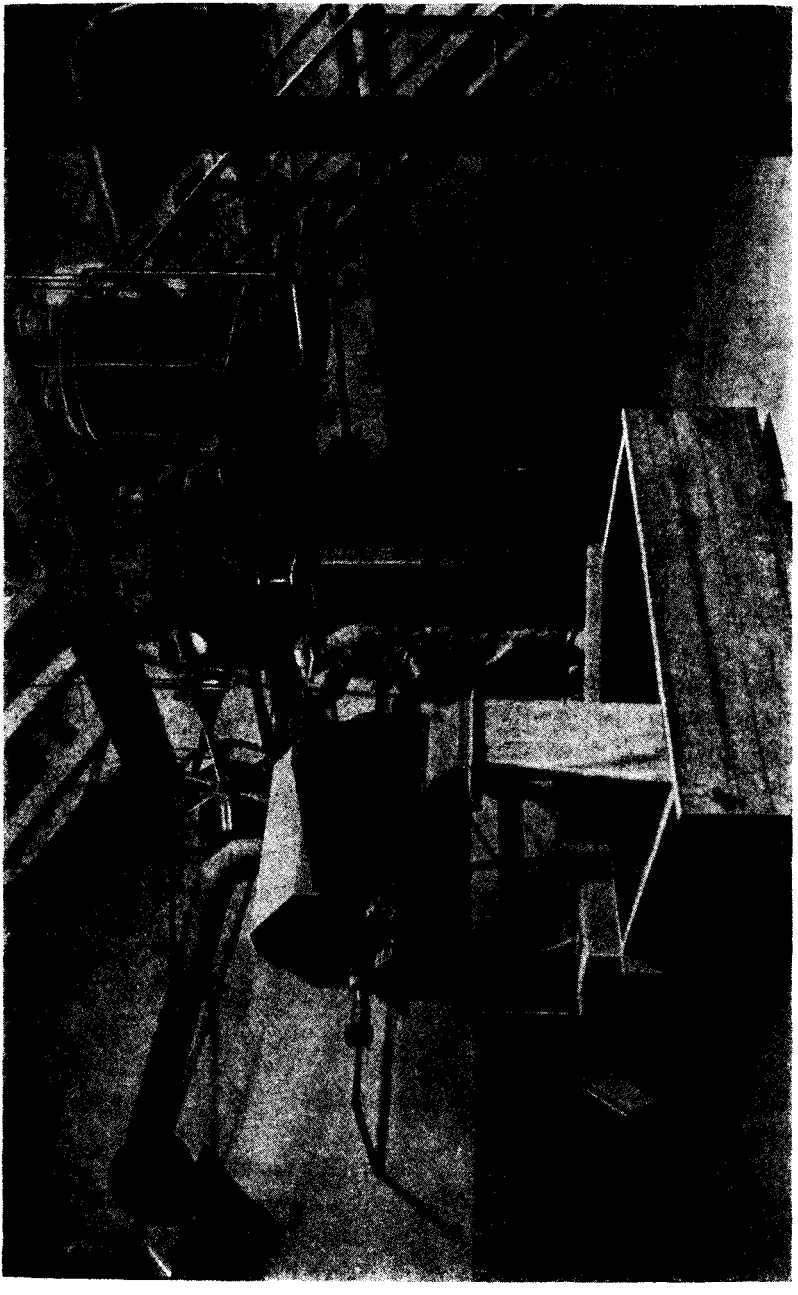


FIG. 95. General view of drying and flaking TNT (Bofors Nobelkrut).

together to form a unit. It is divided into sections by vertical walls, each section consisting of two parts: a larger one for mixing the TNT with water (mixers), and a smaller one for separating both phases (separators).

The vertical walls are provided with holes to allow both molten TNT and water to flow through. Each segment is also provided with horizontal perforated iron plates. The mixers are equipped with stirrers, rotating at high speed, which can direct the contents of the unit upwards or downwards.

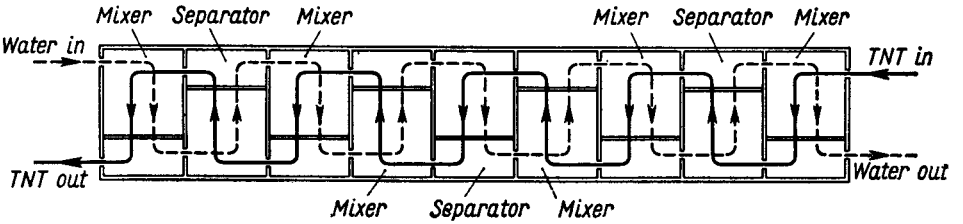


FIG. 96. Continuous washing of TNT (British method [6]).

It can be seen from the diagram that the molten TNT to be washed flows in counter-current against a stream of hot water. In the mixers, emulsification of the TNT in water takes place. The emulsion then passes through an overflow at the top or at the bottom of the mixer (depending on the direction given by the stirrer) to the separator, where the TNT collects at the bottom and flows to the adjacent mixer by an outlet near the bottom. Water rises to the top of the separator and passes in counter-current through an overflow to another mixer. By direct steam heating a temperature 80-100°C is maintained in the trough. The cover of the latter is provided with vent ducts for escaping vapours.

For 1000 kg of TNT about 2500 1. of water is used. The output amounts to 1.5 tons of TNT per hour. After washing the acidity of TNT falls to 0.1-0.2% of H_2SO_4

The sulphitation of TNT is carried out in a unit illustrated in Fig. 97.

The granulated, crude TNT is washed with hot water in a wooden vat A, equipped with a stirrer rotating at a speed of 75 r.p.m., and with a sheet metal lid connected to a ventilating pipe. The mixture in the vat is heated by steam introduced through a silicon-iron pipe. The acidity of the TNT falls after washing to below 0.1% of H_2SO_4. The number of washing operations depends on the initial acidity.

The molten, deacidified TNT is drained off to a crystallizer, placed below. The crystallizer consists of a wooden cylindrical vessel, 0.9 m high and 2.8 m in diameter, equipped with a wooden stirrer.

For crystallization the molten TNT is run from vessel A into a crystallizer filled with water, heated to 90-100°C. The ratio of water to the TNT should be 1:1 by volume. The content of the crystallizer is allowed to cool. At about 75°C the TNT begins to crystallize. After the temperature has fallen to 50°C (in about 4 hr from the time the crystallizer was loaded) sodium sulphite solution is added and the mixture is allowed to react for half an hour at a temperature of 40-45°C. The concentration of Na_2SO_3 in the crystallizer is 34%. The weight of the Na_2SO_3

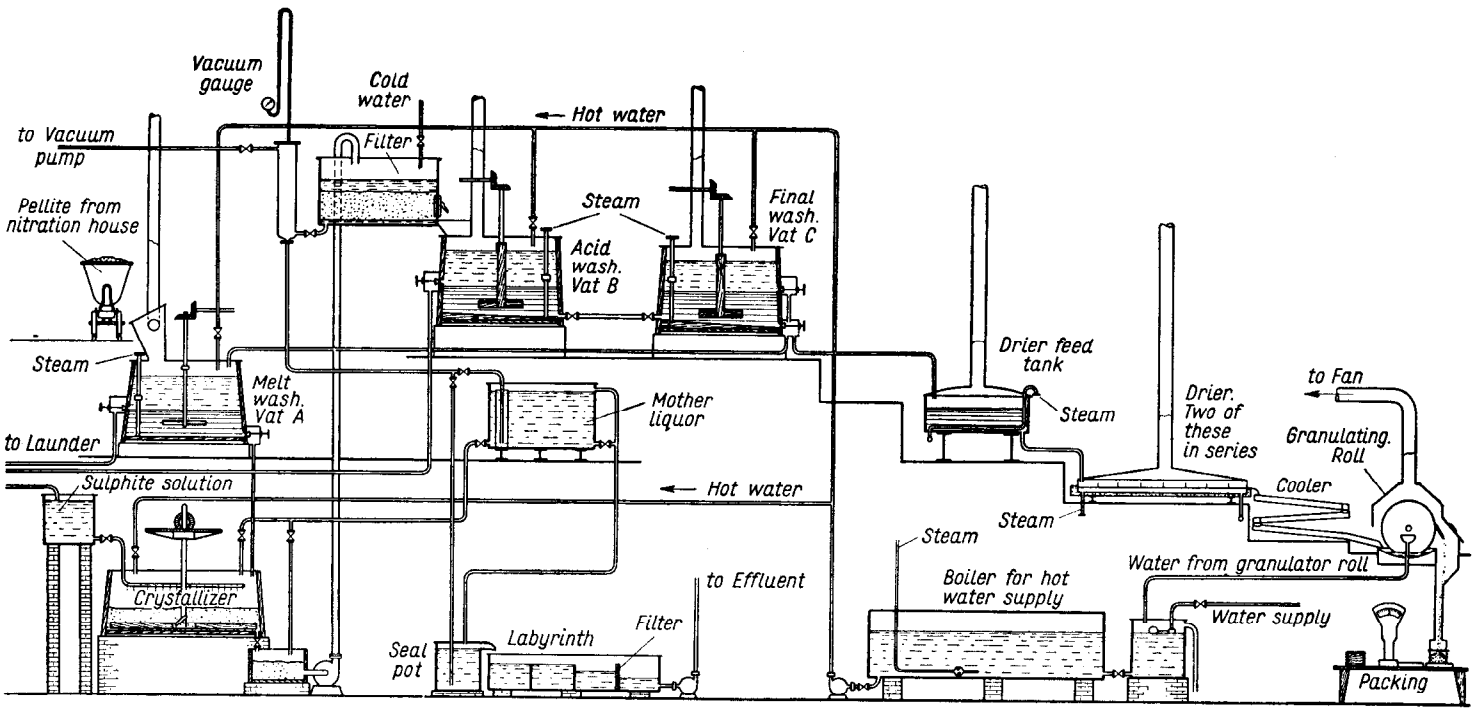


FIG. 97. Sulphitation of TNT (British method [6]).

used amounts to 3.54% of the weight of the TNT. The designers of this method believe that the uniform, Ime crystals formed in the crystallizer are most suitable for the sulphitation process.

The suspension of crystals in sodium sulphite solution is pumped upwards by a rotary pump to a vacuum filter through a small tank in which the suspension is diluted with water. After the TNT has been separated from the liquor it is washed with cold water until its pink colour, produced during the sulphitation process, disappears. The aluminium filter plate in the filter bowl should be covered with linen cloth, which in turn is covered with a layer of pure, granulated TNT.

After sulphitation and washing, the TNT is transferred to tank *B,* containing water acidified with sulphuric acid (up to 0.1%). Here the TNT is freed from any traces of basic sodium sulphite. The acidified, molten TNT is then transferred to tank C for final washing with pure, hot water. The washing is repeated several times, until the wash water proves neutral.

The solution of sodium sulphite from filtration of the TNT is collected in an intermediate tank from which part may be directed back for the sulphitation and part to a settling tank (labyrinth). There a certain amount of TNT slurry sets and may be utilized as the grade III TNT.

The washed TNT is then transferred to a tank where it is kept in the molten state and thence through a bronze wire gauze (for retaining any impurities) it is poured in a thin layer on to a tray for drying. The tray is steam heated to keep the TNT at a temperature of 105-115°C. Due to this temperature and the thin layer of the product, drying takes only a short time. Free from moisture, hot TNT is allowed to flow via a spout (in which it is cooled to about 98°C) into a flaker. The drum and the knife of the flaker are made of bronze. The drum is 60 cm in diameter and is rotated at a speed of about 4.5 r. p. m. (Fig. 94).

All pipes for conveying the molten TNT are heated by steam located below the TNT pipes, both being heat insulated.

German method

In a German method, applied at the Krümmel factory, the crude acid TNT, after it has been washed free from nitrosylsulphuric acid, is washed several times with water at a temperature of 90°C in brick washing vats lined with sheet lead, or in stainless steel tanks. The deacidification is finally followed by neutralization with an $NaHCO_3$ solution of concentration about 1%. The product obtained in this stage has a freezing point of 78.8-78.3°C.

For further purification molten TNT and hot water in equal volumes are run into a cast iron tank of 15 m^3 capacity, where the TNT is emulsified by vigorous stirring. The emulsion is cooled to 74-76°C and treated with a 25% solution of sodium sulphite, used in such a proportion as to obtain a final concentration of sodium sulphite in the mixture of 2.5%. During the sulphitation process 5-6% of trinitro compounds and 0.2-0.3% of tetranitromethane (calculated on the TNT) go into solution.

After half an hour the stirrer is stopped, the solution is separated by decantation and the TNT left behind is washed with water again at 85-90°C. If TNT of very high purity is required (m. p. 80.6%) it is sulphitated once more with a 0.5% solution of sodium sulphite.

The washed TNT is then air dried in a water heated tank of capacity 15 m^3, at 85-90°C. At this stage of manufacture samples are taken for determining the freezing point of the product. Finally the dry TNT is flaked on a steel drum with a bronze knife.

Continuous methods

Continuous washing with sodium sulphite was also applied at Schlebusch (Fig. 98).

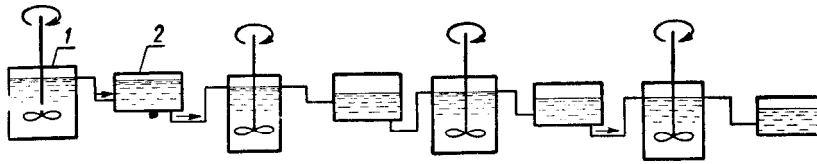


FIG. 98. Continuous washing with sodium sulphite of TNT in Schlebusch (CIOS XXIV - 4).

The purifying unit consisted of four washing tanks (I) and four separators (2). As in the nitration plant the vessels were arranged in cascade. The first washing tank was for washing the TNT with water, the next one for washing with sodium sulphite and the last two again for washing with water. Each was 0.5 m high and 0.8 m in diameter.

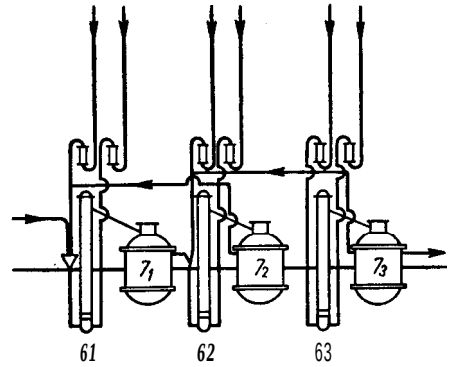


FIG. 99. Meissner's continuous process of washing nitrotoluenes including TNT (co-currentsounter-current method [20]).

Meissner's continuous process for washing nitrotoluenes, applied also for TNT (Fig. 99), belongs to the co-current-counter-current type. The quantity of water used should be as small as possible, thus reducing the losses of nitrotoluenes to

a minimum. The nitro compound, separated from acid in the separator (4) (see the diagram in Fig. 87) flows to the washing column (6,), fed with fresh water. A mixture of the nitro compound and water flows off at the top of the column to the separator (7_1), where the nitro compound separates from acid washings. The washings (being the upper layer in the separator) are drained away, while the nitro compound flows to the next column (6_2), fed with the water from the third separator (7_3). A calculated weight of alkali is added to column (6_2) to neutralize any acid present. The neutralized mixture of the nitro compound and wash water flows off at the top of column (6_2) to separator (7_2) The water separated from the nitro compound is drained away while the nitro compound is transferred to column (6_3), whence it overflows to separator (7_3.) The nitro compound from the third separator passes to further nitration or to a drier, while water is led to column (6_2)

The equipment is made of stainless steel, those parts that hold alkaline or neutral liquids may be made of carbon steel. The washing columns are equipped at the bottom with air injectors for emulsifying the nitro compounds in water. To avoid any hazards the plant is not equipped with mechanical stirrers.

To remove any acid present the TNT is water-washed, neutralized with a solution of sodium hydrogen carbonate, then with a solution of sodium sulphite and finally washed several times with water.

SCHEMATIC DIAGRAM OF A PLANT FOR CONTINOUS TNT MANUFACTURE

A schematic diagram of such a plant is shown in Fig. 100. Separate buildings are denoted :

1. Packing department
2. Granulation
3. Sulphite washing and TNT drying
4. TNT washing
5. Nitration of nitrotoluene to di- and tri-nitrotoluene
6. Absorption
7. Concentration of sulphuric acid
8. Concentration of nitric acid
9. Preparation of washing solutions
10. Compressor house
11. Boiler house
12. Acid storage tanks for di- and tri-nitrotoluene
13. Acid storage tanks for mononitration
14. Distillation and mononitrotoluene separation plant
15. Toluene and mononitrotoluene separation tanks
16. Mononitration plant
17. Mononitrotoluene washing plant
18. Safety embankments
19. Safety walls for shielding passages.

A schematic diagram of a plant operated by the A. B. Bofors system is shown in Fig. 101.

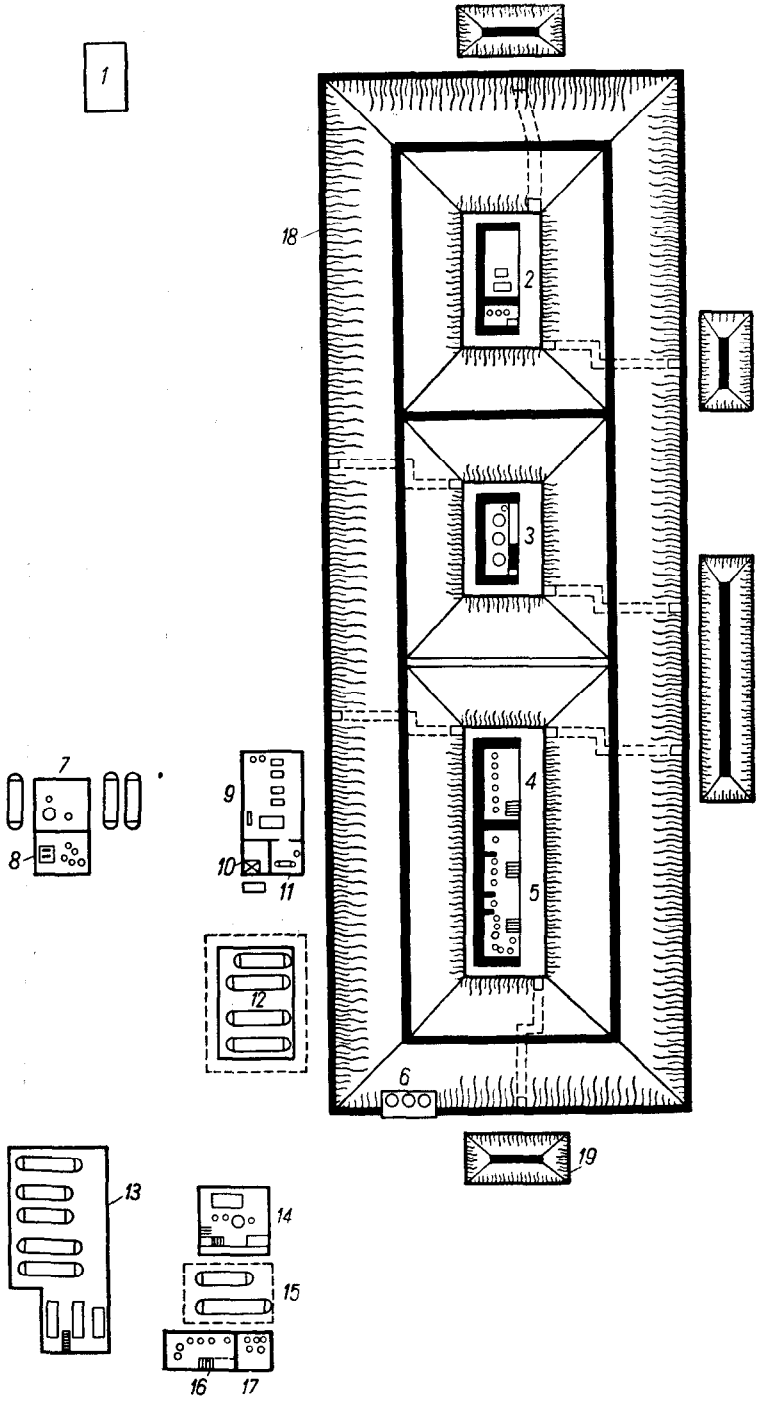


FIG. 100. Lay-out of a plant for continuous TNT manufacture according to Meissner [20].

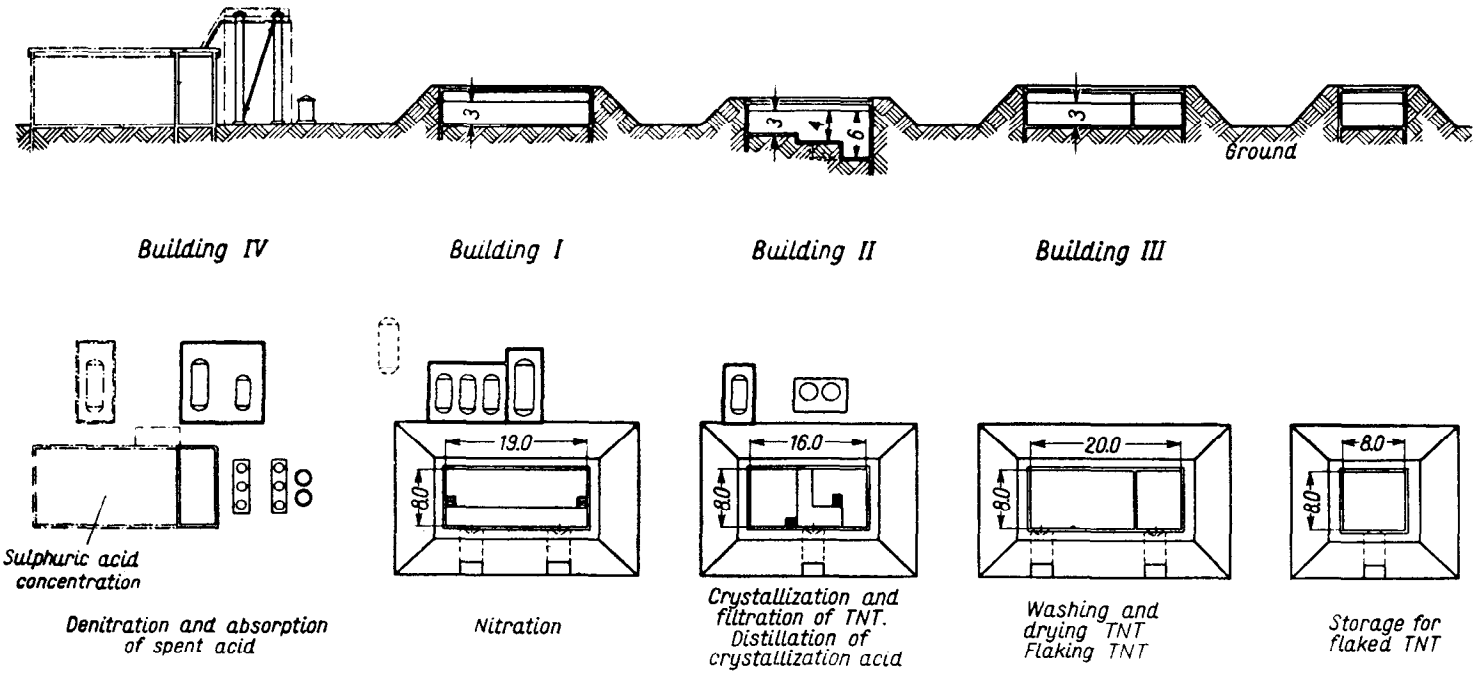
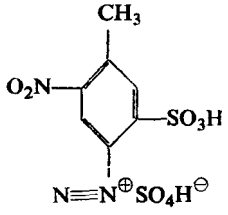


FIG. 101 Lay-out of a Bofors plant for continuous TNT manufacture [17]. (Dimensions in meters).

UTILIZATION AND NEUTRALIZING OF SULPHITATION LIQUORS

The sulphitation liquors contain dinitrotoluenesulphonic acids in a quantity amounting to about 4% of the TNT produced. In a period of intensive manufacture of TNT this may be of considerable importance from an economic point of view. This is why the problem has arisen of how to utilize the organic compounds contained in sulphitation liquors.

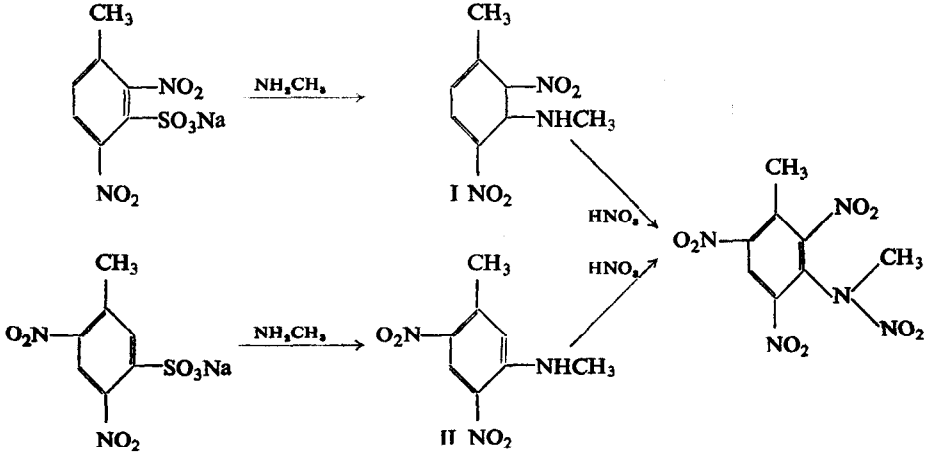
Batik [27] found that the acidification of sulphitation liquors with an inorganic acid resulted in the formation of $NaHSO_3$, which reduced the nitro- to the amino group. Simultaneously, due to the presence of $NaNO_2$, diazotization took place and a red diazonium salt



was precipitated.

The compound may be utilized for further reactions, for example in dyestuffs manufacture.

British Technical Records [6] mentioned another approach to the problem of utilization of sulphitation liquors. According to these data, attempts were made in Great Britain during World War I to make use of the reactivity of the sulpho group in the *ortho* or *para* position to the nitro ones. By acting with methylamine, N-methyldinitrotoluidine (I and II) was obtained, which, when further nitrated, yielded "methyltetryl". All the methods mentioned proved uneconomical.



Gornall and R. Robinson [28] suggested reducing sodium dinitrotoluene sulphate (e.g. the sodium salt of 2,4-dinitrotoluene-3-sulphonic acid) to yield *m*- toluene-diamine-3-sulphonic acid which could serve as an intermediate for obtaining azo dyes. Oxidation of sodium 2,4-dinitrotoluene-3-sulphonic acid with potassium permanganate in alkaline medium gave 2,4-dinitro-3-sulphobenzoic acid, also an intermediate for azo dyes.

WASTE WATERS

The problem of the neutralization of waste water from the manufacture of TNT, and the possibility of utilizing the dinitrotoluenesulphonic acids present in them acquired a considerable importance during World War II, owing to the enormous output of TNT. In Germany alone the production of TNT was over 20,000 tons a month, whereas during the World War I it averaged merely 3000 tons a month.

Such a high output involved the use of tremendous quantities of water. According to Kratz [29], for an production of TNT of 4000 tons monthly, 40,000 m^3 of water were used daily. Most of this was used for cooling, while the quantity of waste water containing nitro compounds and acids amounted to 5000-6000 m^3. Kratz believed this consumption of water to be abnormally high, and caused by hasty production.

Kratz has classified the "acid" waters according to their origin as follows (Table 87):

TABLE 81

Origin of water	Output m^3/hr	Colour and appearance	Acid content	Colour after purification with lime milk
Process water	50	brick-red turbid	4 g/l. H_2SO_4 2 g/l. HNO_3	dark red
Condensed water from concentration of sulphuric acid	100	almost Colourless, clear	2 g/l. H_2SO_4 0.3 g/l. SO_2	pale pink
		from light to dark brown	5 g/l. H_2SO_4	dark red
Wash water	80	from clear to turbid, with suspension	2g/l. HNO_3 (changeable)	

Channels for discharging waste water should be open gutters or loosely closed troughs. The channels should be built of acid resistant bricks, joined by asplit (phenolic resin).

The removal of dinitrotoluenesulphonic acids from waste waters prevents a difficult problem since due to their high solubility they are difficult: to absorb on carbon or on anion exchangers, or to extract with dibutyl phthalate.

The water may be decolourized by chlorination, but this requires large quantities of chlorine. Biological processes can lead to destruction of TNT, but the sulphonic acids remain unaffected.

For this reason, according to Kratz, the most rational way of removing TNT and salts of nitrosulphonic acids from the water is by simply distilling off the water and then destroying the non-volatile residue.

Since this method is expensive as regards capital and operating costs, Kratz has suggested a method of treatment for acid waste water from the TNT manufacture consisting in agitating with 5-10% milk lime.

The reaction with calcium hydroxide is rather slow, so agitation should go on for some time (5-15 min). The mixture is then allowed to remain at rest for clarification. Treatment with milk of lime neutralized the acids and caused the precipitation of several coloured compounds, among others the products of the reaction of trinitrotoluene with calcium hydroxide. The amount of calcium oxide consumed in the process is 700 tons monthly, at an output of 4000 tons of TNT a month.

SAFETY IN TNT MANUFACTURE

The manufacture of TNT is one of the safest operations in the explosive industry. Nevertheless, any negligence about safety regulations may have disastrous consequences. Because the manufacturing process is regarded as safe, the fact must not be overlooked that less experienced personnel may disregard the regulations.

The most hazardous operation in TNT manufacture is nitration, primarily mono- and tri-nitration. In mononitration the hazard is due to the extremely violent reaction of the unreacted hydrocarbon with the nitrating mixture, and to the fact that nitro derivatives of cresols are formed in the process, along with nitrotoluenes. The last stage - trinitration - is dangerous due to the drastic conditions of the reaction which requires concentrated acids and a high temperature. The earlier method of trinitration at which temperatures up to 120°C were applied, was particularly hazardous. If the mononitrotoluene has not been freed from nitrocresols, trinitration is still more dangerous, due to the high reactivity of nitrocresols, and their liability to undergo oxidation. The formation of carbon monoxide may also be a cause of an explosion in the course of trinitration [33] (p. 339).

The spent acid from trinitration has also been the cause of several disasters, although it had been considered safe to handle. The most noteworthy example of this occurred in the Reinsdorf factory in Germany in 1935. The hot spent acid flowed down to open iron tanks, where, as the liquid cooled, a mixture of di- and Tri-nitrotoluenes rose to the surface. It was skimmed off from time to time and transferred to a washing tank, where it was washed with water. On skimming, a rubber glove and a shelf left on the brim of the tank with some cotton wool on it, fell into the tank. The reaction between the spent acid and the rubber and cotton wool initiated violent decomposition and fire. An attempt to extinguish the flames failed,

and soon the nitro compounds on the surface of the spent acid exploded. The explosion and fire spread over several nearby tanks, then to the nitro compounds in the washing tank. As a result the whole plant for the recovery of nitro compounds was destroyed. In addition to this the explosion tore away the roofs of some nearby buildings, among them drier buildings located at a distance of about 660 m. Parts of the tank thrown off by the explosion into one of the driers detonated the TNT present, and in another they caused the ignition of the load. Similar explosions or fires spread over further buildings of the TNT factory. Moreover, a neighbouring nitroglycerine plant also exploded. This disastrous explosion cost 82 human lives and in addition 104 people were seriously and 700 were lightly injured.

Accidents caused by spontaneous explosion of finished TNT are also known. Some of them could be ascribed to the presence of traces of trinitrocresol salts. Others were presumably caused by products of decomposition of trinitrotoluene under the influence of sunlight or alkaline compounds used for deacidification of the TNT. Still others were due to the high sensitiveness of molten TNT to impact. This is why the drying of TNT should be regarded as a very dangerous operation.

Descriptions of several explosions that took place in French factories, may be very instructive. As an example, the explosion in the St. Chamas TNT factory in 1936 which caused the death of 53 people. Investigations showed that the explosion occurred after about 2000 kg of TNT in a drying tank had caught fire. The TNT in question was that recovered from the spent acid from trinitration ("plastic TNT"). It is known that such a product contains various impurities, among them the isomers of α– trinitrotoluene, nitrocresols etc. It had first been washed with water at 90°C then with a 6% solution of sodium carbonate, and again with water. The drying was effected at 85°-90°C by passing air for 8 hr. In the case described, as the drying TNT still contained some acid, 7 kg of sodium carbonate (i.e. 0.35% in relation to TNT weight) were added to the tank with the drying TNT which at the time contained only a very small quantity of water. This must have led to the formation of typical decomposition products of TNT brought about by reaction with alkalis. It is highly probable that these compounds were the first to ignite. whereupon the flames spread over the whole drier.

A number of explosions in French TNT factories which occurred during 1917-18, in particular the one at Neuville-sur-Saone (1917) which caused the destruction of the whole plant, were presumably due to the decomposition of the products of reaction of metals, such as lead or iron, with TNT under the conditions described in a paper by Kovache and Thibon [31]. Products readily decomposed, and sensitive to friction and impact, were formed in various parts of the plant where contact between these metals and the TNT could occur in the presence of dilute nitric acid, for example in the TNT washing tank and granulators. Similar compounds were found in a nitrator where part of the TNT in close contact with metals was subjected to the action of nitric acid vapours, for example around the seals at the stirrer shaft bearings.

Similar compounds were also found in an iron sulphitation tank. TNT is in-

flammable, although this occurs under specific conditions of prolonged action of glowing material.

Steele [32] described the following accident in the amatol section of an ammunition factory. A worker smoking a cigarette (in spite of the regulations) threw it away when he saw a foreman coming up. The burning cigarette fell on a sack filled with TNT. After a while the jute sack caught fire causing the TNT to ignite, and then to explode. This involved the explosion of the amatol in a mixer located in the same premises. The explosion tore away the wooden roof, and its fragments scattered on to other buildings causing further explosions. Soon all buildings of the factory were on fire and destroyed and 11 lives were lost, mainly in fire fighting.

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CHAPTER X

NITRO DERIVATIVES OF HIGHER BENZENE HOMOLOGUES

HIGHER benzene homologues, which have more or longer side chains than toluene, undergo oxidation more readily during the nitration process than toluene or benzene. They should therefore be nitrated with great care; the higher homologues in particular should be nitrated at a temperature as low as possible. As a rule the range of permissible concentrations of nitrating acids is narrower than for nitration of benzene or toluene. An excess of nitric acid should also be avoided. For example Kobe and Langworthy [1] gave the following data on the nitration of *p*- cymene to the mononitro derivative. An 89% yield can be obtained by nitration at 10°C, with a mole ratio of nitric acid to *p*- cymene of 0.9 and a weight ratio of sulphuric acid to *p*- cymene of 4.0, initially using a sulphuric acid concentration of 85 weight % and very vigorous stirring.

NITRO DERIVATIVES OF XYLENES

m- Xylene is the most important of the three xylene isomers *(ortho-, meta-* and *para-)* as a starting material for the preparation of nitro derivatives, as it enables three nitro groups to be introduced into the 2-, 4, and 6- positions. *Ortho-* and *para-* xylenes can give a stable system when only two nitro groups are introduced, for when three groups are introduced one of them is compelled to occupy an inappropriate position and may easily undergo substitution reactions.

Xylene for nitration should therefore be as rich in the *m*- isomer as possible. The requirements for the nitration of xylene will be discussed on pp. 406-412.

The presence of two methyl groups on the benzene ring greatly facilitates the introduction of nitro groups. In consequence less concentrated mixtures may be used for the preparation of trinitro-m-xylene (TMX) than for TNT.

On the other hand, the methyl groups are easily oxidized so the nitration should be married out under conditions less favourable for oxidation, for example at a temperature as low as possible. Low concentration of the nitrating mixture also facilitates oxidation reaction of xylene. Gorst [2] reported that the rate of oxidation is reduced with increase in the factor Φ or concentration of H_2SO_4 in nitrating

mixtures. This can be seen in the diagram (Fig. 102) illustrating the nitration of DNX to TNX. The quantity of N_2O_3 evolved during the reaction was taken as a criterion of the intensity of the oxidation reactions.

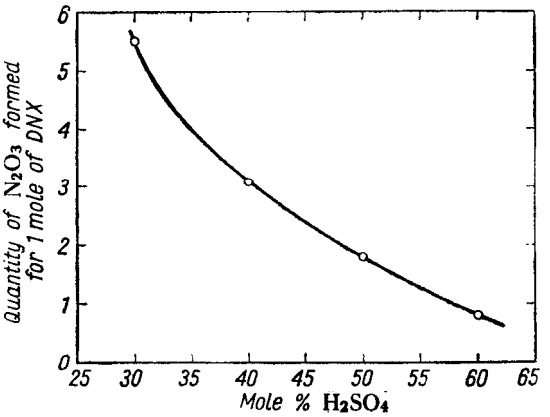


FIG. 102. Oxidation of dinitroxylene as a function of the concentration of sulphuric acid in nitrating mixtures (Gorst [2]).

Ortho- and *para-* xylenes are particularly easy to oxidize. One of the reasons why TNX has not been more widely used as explosive is that it is difficult to isolate m-xylene from the corresponding light oil or petroleum fractions (p. 406). Owing to the presence of its isomers commercial m-xylene, when nitrated, gives a mixture of nitro compounds, often containing oily components that exude easily and which are highly undesirable where a high purity product is required (e.g. for filling shells). In addition to this, trinitro-m-xylene has other disadvantages, viz.: its high melting point, which makes it difficult to fill shells by pouring, and its relatively low explosive power, which corresponds approximately to that of dinitrobenzene. An advantage of TNX is its low toxicity.

In spite of its drawbacks, during World War I France, Russia, and the United States used commercial trinitroxylene as an explosive, mostly in mixtures with other nitro compounds, or with ammonium nitrate, when these countries were short of nitration grade toluene. In the period between the two World Wars trinitroxylene was manufactured in the U.S.S.R and France and on a small scale in Poland.

Trinitroxylene is known as Ksilil (U.S.S.R.), Xylite (France), Ksylit (Poland) and TNX.

The commercial product, according to Kravchinskii [3], melts partially at 120-125°C and completely at 160-177°C, and solidifies at 160-162°C, while chemically pure 2,4,6-trinitro-m-xylene melts at 182°C.

The grades of commercial TNX as classified by their melting points are:

I grade	m. p.	170°C
II grade	m. p.	160-162°C

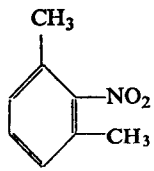
In addition grade III trinitroxylene may also be available. This is an oily product used like nitrated solvent-naphtha, for special purposes (e.g. in coal mining explosives).

Nitro derivatives of xylene were first mentioned in a work by Bussenius and Eisenstück [4], in 1860, on various products obtained from petroleum. The authors investigated among others the Hannover oil fraction, boiling from 75°C to 180°C. This fraction contains easily nitrated aromatic hydrocarbons. Among the products obtained in nitration, there was a crystalline compound melting at 169°C of composition, corresponding to that of trinitroxylene, as confirmed by analysis. A similar substance of higher purity, melting, at 177°C was obtained by Beilstein [5] in 1864 by nitration of xylene.

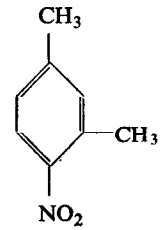
Systematic studies of the nitration of xylene and of the constitution of the products obtained were carried out by Noelting and Fore1 [6] and Blanksma [7]. During World War I in Russia Solonina [8] and Filippov [8a] and in France Marqueyrol and Loriette [9] developed methods of preparing nitroxylene in an industrial scale.

ISOMERS OF MONONITRO-m-XYLENE (MNX)

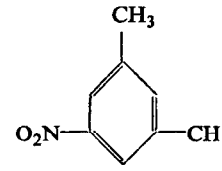
Three isomers of mononitro-m-xylene are known, viz.: 2-,4-, and 5-nitro-m-xylenes :



b. p. 225.5°C



m. p. 2°C
b. p. 246°C



m. p. 74°C
b. p. 273.7°C

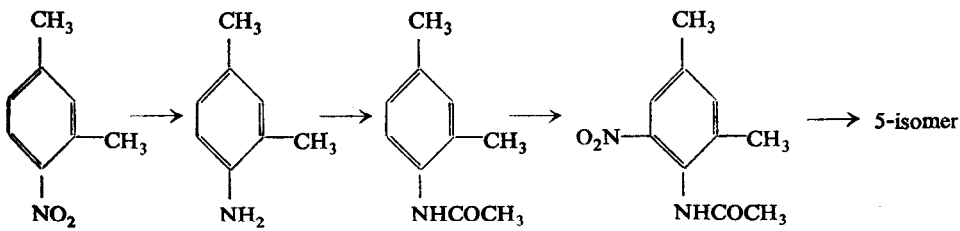
All three isomers can be obtained by nitrating m-xylene using a nitrating mixture of the composition:

HNO_3	25-28%
H_2SO_4	56-59%
H_2O	16%

The nitration temperature should not exceed 35-40°C.

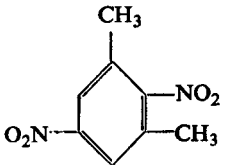
The principle products are the 2- and 4-isomers in the proportion of 25:75, while the 5- isomer is obtained only in an insignificant quantity.

The latter can be obtained from the 4- isomer (Wróblewski [46]):

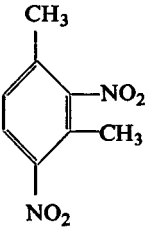


ISOMERS OF DINITRO-m-XYLENE (DNX)

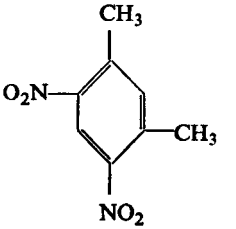
The following three isomers of dinitro-m-xylene are known:



m. p. 132°C



m. p. 82-84°C



m. p. 101°C

All three isomers can be obtained either by the nitration of *m*- xylene with a nitrating mixture such as:

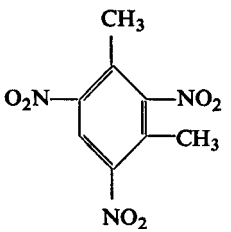
HNO_3	20%
H_2SO_4	65%
H_2O	15%

or by the nitration of mononitro-m-xylene with a mixture poorer in nitric acid (e.g. HNO3 - 10-12%, H_2O - 15%).

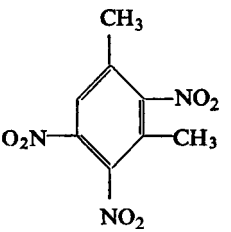
The 2- isomer predominates in the nitration product, while the 2,5- isomer formed in the nitration of 5-nitro-m-xylene is obtained only in small quantity.

ISOMERS OF TRINITRO-m-XYLENE (TNX)

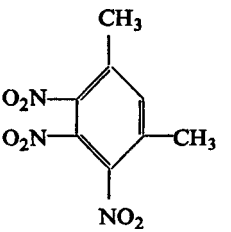
There are three isomeric trinitro-m-xylenes: 2,4,6-trinitro-m-xylene, 2,4,5-, and 4,5,6-trinitro-m-xylene :



m. p. 182°C



m. p. 90°C



m. p. 125°C

The 2,4,6- isomer is the principal component of the products of nitration of *m*- xylene. It constitutes the largest part of the purified commercial product. The 4,5,6- isomer is formed only in an insignificant quantity.

The composition of the nitrating mixture depends on whether *m*- xylene, nitro- or dinitro-m-xylene is to be nitrated. Usually more dilute mixtures are applied than for the nitration of toluene to trinitrotoluene.

For example, for the conversion of dinitro- to trinitro-m-xylene, a mixture containing 9-10% of water at a temperature up to 100°C is used.

m- Xylene can be nitrated to its trinitro derivative in one stage using a nitrating mixture containing ca. 20% of HNO_3 and ca. 3% of H_2O.

Physical properties of 2,4,6-trinitro-m-xylene

2,4,6-Trinitro-m-xylene crystallizes in white crystals at room temperature. It is only slightly soluble in concentrated sulphuric acid - at a temperature of 150-160°C 10% of it goes into solution. In fuming sulphuric acid the solubility is higher.

The solubility of 2,4,6-trinitro-m-xylene in organic solvents is much lower than that of α– trinitrotoluene (Table 88).

TABLE 88

SOLUBILITY OF 2,4,6-TRINITRO-m-XYLENB IN ORGANIC SOLVENTS

Solvent	At room temperature g/100 ml of the solvent	At boiling point g/100 ml of the solvent
Benzene	0.5	7.5
Toluene	0.5	20.5
Alcohol	0.05	0.55

The solubilities of trinitro-m-xylene (m. p. 180.5°C) in mixtures of benzene with alcohol (after Kravchinskii [3]) are given below (Table 89).

TABLE 89

SOLUBILITY OF TRINITRO-m-XYLENE IN MIXTURES OF BENZENE WITH ALCOHOL

Composition of the solvent, parts by volume		Solubility, g/100 ml of the solvents	
benzene	alcohol	at 8 ° C	at 20°C
1	0.5		0.71
1	1	0.32	0.45
1	1.5	0.24	0.29
1	2	-	0.2

At high temperatures 2,4,6-trinitro-m-xylene is readily dissolved by acetic acid and by aniline. 2,4,6-Trinitro-m-xylene forms eutectics with aromatic hydrocarbons and their nitro derivatives. Some of the available data are tabulated (Table 90).

The steam volatility of 2,4,6-trinitro-m-xylene is low. At a temperature of 100°C it begins to sublime. It can be purified by sublimation at 150-170°C. The thermal conductivity of 2,4,6-trinitro-m-xylene at 25°C is 0.00057 (Prentiss [12]).

chemical properties of 2,4,6-trinitro-m-xylene

2,4,6-Trinitro-m-xylene is not affected by hot concentrated sulphuric and hydrochloric acids, but it reacts with alkalis in the presence of alcohol or acetone, yielding an intense blue addition product.

2,4,6-Trinitro-m-xylene forms addition products less easily than α– trinitrotoluene. Undoubtedly the two methyl groups present in the ring reduce its ability to form addition compounds.

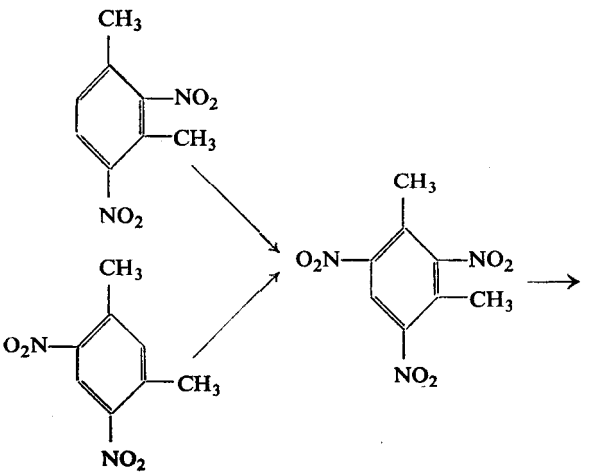
TABLE 90

EUTECTICS WITH 2,4,6- TRINITRO-m-XYLENE

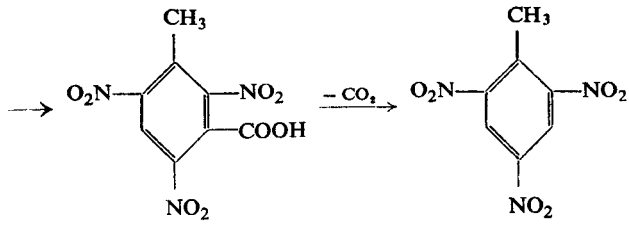
The second component	% TNX by weight	m. p. °C	Authors
Anthracene	64.4	151.2	Jefremov and Tikhomirova [10]
m- Dinitrobenzene	17.8	76.4	
2,4-Dinitrotoluene	6.0	67.7	Bell and Sawyer [11]
Naphthalene	7.6	76.0	Jefremov and Tikhomirova [10]
p- Nitrotoluene	2.0	50.5	Bell and Sawyer [11]
Picramide	23.5	110.8	Jefremov and Tikhomirova [10]
Picric acid	21.7	105.8	"
Picryl chloride	12.8	73.2	"
Tetryl	23.5	110.8	"
sym-Trinitrobenzene	16.4	104.6	"
	(Solid solution, system V of Roozeboom)		
2,4,6-Trinitro-m-cresol	17.2	84.6	Jefremov and Tikhomirova [10]
Trinitroresorcinol	37.5	141.3	,,
2,4,6-Trinitrotoluene	8.0	75.2	,,
	(Solid solution, system V of Roozeboom)		

According to Jefremov and Tikhomirova [10], 2,4,6-trinitro-m-xylene contrary to both sym-trinitrobenzene and 2,4,6-trinitrotoluene does not combine with such hydrocarbons as acenaphthene, anthracene, phenanthrene, fluorene or naphthalene.

The constitution of 2,4,6-trinitro-m-xylene was determined by Grevingk [13]. He nitrated both 2,4- and 4,6-dinitro-m-xylene and obtained the same product.

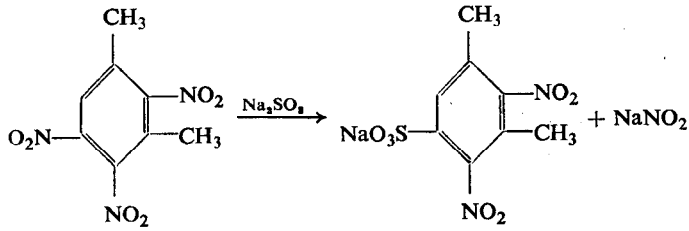


(1)



Then, by oxidizing one of the methyl groups to a carboxyl group with chromic acid, he obtained a carboxylic acid which on losing CO_2 was converted to α– trinitrotoluene.

The isomers of 2,4,6-trinitro-m-xylene formed in the nitration process may of course be removed from the product by crystallization or by reacting with sodium sulphite, the substitution of a nitro group by a sulpho group taking place, e.g.:



(2)

The reaction proceeds much more slowly than with the unsymmetrical trinitro derivatives of toluene.

Explosive properties of 2,4,6-trinitro-m-xylene

2,4,6-Trinitro-m-xylene is more sensitive to impact than TNT. This can be explained by the presence of a large number of substituents on the benzene ring. As Wohler and Wenzelberg [14] found, it could explode at only about half the impact energy needed for the explosion of TNT.

Other authors, however, declare that the sensitiveness of trinitro-m-xylene is only slightly higher than that of TNT. Taking 100 as figure for picric acid, the sensitiveness of TNT is 127 and that of trinitro-m-xylene is 120.

The explosive properties of trinitro-m-xylene, as measured by Kravchinskii [3] are: initiation temperature, 330°C; lead block expansion test, 270 ml (for TNT this author gives 285 ml); rate of detonation, 6600 m/sec (d = 1.51).

Kast [15] found the explosive power of 2,4,6-trinitro-m-xylene to be similar to that of *m*- dinitrobenzene.

The heat of formation of 2,4,6-trinitro-m-xylene equals +18.3 kcal/mole.

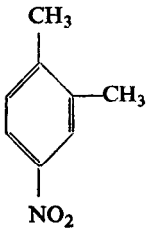
Applications of TNX

Trinitroxylene is used as an additive for fusible explosive compositions mixed with TNT, with TNT and picric acid, or with ammonium nitrate (Vol. III). For the compositions of various eutectics with trinitroxylene see p. 400.

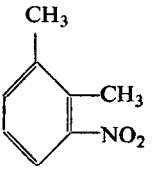
MONONITRO DERIVATIVES OF *o*- AND *p*- XYLENES

Ortho- and *p*- xylene nitrate more readily than *m*- xylene. They are also more readily oxidized especially during mononitration as well as during vigorous nitration to trinitro derivatives. For this reason the yields obtained in the nitration of *o*- and *p*- xylene are lower than those obtained with *m*- xylene.

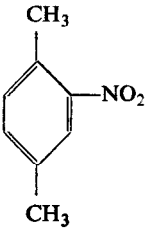
The following mononitro derivatives are known: 4-nitro- and 3-nitro-o-xylene and 2-nitro-p-xylene :



m. p. 30°C
b. p. 258.8°C



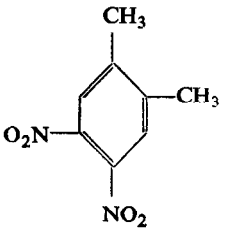
m. p. 9%
b. p. 250-8°C



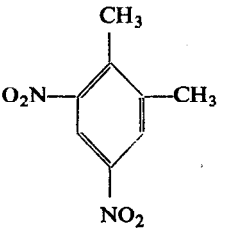
b. p. 234-239°C

DINITRO DERIVATIVES OF *o*- AND *p*- XYLENES

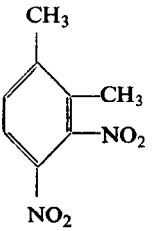
The following dinitro-o-xylenes are known: 4,5-, 4,6- (or 3,5-), 3,4- and 3,6- *o*- xylene :



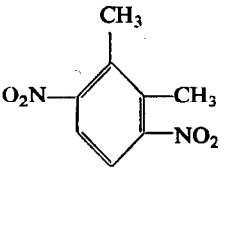
m p. 115°C



m. p. 75-76°C

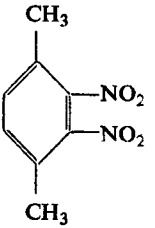


m. p. 82°C

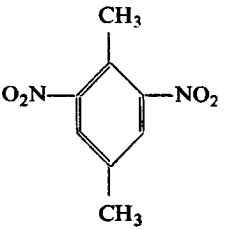


m. p. 56-60°C

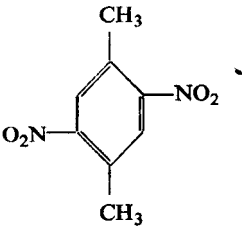
Among dinitro derivatives of *p*- xylene the following three isomers are known : 2,3-, 2,6- and 2,5-dinitro-p-xylene :



m. p. 93°C



m. p. 123-129.5°C



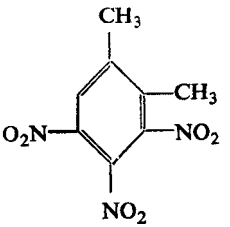
m. p. 147-148°C

Nitration of *p*- xylene mostly yields the 2,3- and 2,6-isomers.

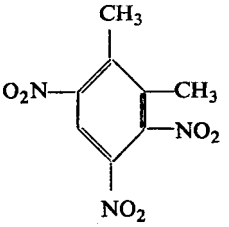
TRINITRO DERIVATIVES OF OF AND *p*- XYLENES

At first *o*- xylene was believed (Noelting and Thesmar [16]) to be without trinitro derivatives, until Crossley and Renouf [17] obtained a trinitro compound,

which they separated into two isomers - 3,4,5- (or 4,5,6-) and 3,4,6- (or 3.5,6-):



m. p. 115°C

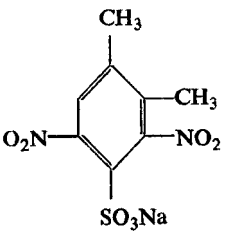


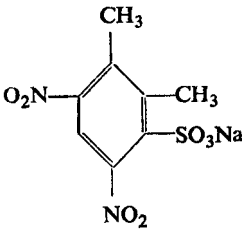
m. p. 72°C

Later these observations were confirmed by Marqueyrol and Loriette [9]. From 100 parts of *o*- xylene, 130-135 parts of trinitro derivatives are obtained.

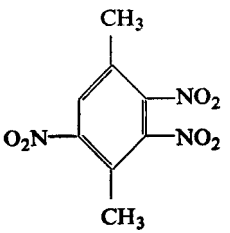
To separate the isomers use is made of their different solubility in 75% sulphuric acid. The mixture of isomers is dissolved in the acid at 120-130°C, and then cooled; only the 3,4,5-isomer crystallizes then. The 3,4,6-isomer left in the acid can be precipitated from the solution by adding water. The 3,4,5-isomer can be purified by crystallization from 75% sulphuric acid, the 3,4,6-isomer by crystallization from alcohol.

Both isomers react with sodium sulphite to form the corresponding sulpho derivatives :





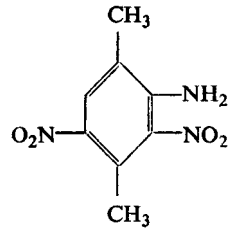
Only one trinitro-p-xylene exists, viz. 2,3,5- or 3,5,6-trinitro-p-xylene :



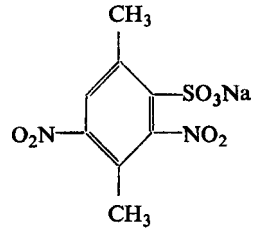
m. p. 139-140°C

It was first obtained by Noelting and Geissmamr [18] in a yield of 150 parts Per 110 parts of *p*- xylene.

With an alcoholic solution of ammonia, trinitro-p-xylene gives dinitroxylidine:



which reacts with sodium sulphite to form a sulpho derivative:



The solubility of the trinitro derivatives of *o*- and *p*- xylene in various solvents is higher than that of trinitro-m-xylene. Here are the comparative data on the solubilities in 100 ml of 95% alcohol at 8°C (after Kravchinskii [3]):

2,4,6-trinitro-m-xylene	0.024 g
3,4,5-trinitro-o-xylene	0.874 g
3,4,6-trinitro-o-xylene	1.159 g
2,3,5-trinitro-p-xylene	0.325 g

MANUFACTURE OF TRINITROXYLENE (TNX)

Xylene

The success of the nitration process, from the point of view of the quality and yield of the product as well as of safety, depends to a considerable extent on the quality of the xylene used. For nitration, both xylene from coal pyrolysis and from petroleum is used. In both cases *m*- xylene is the main component of the crude substance.

The average composition of xylene from coal is:

o- xylene	10% (b. p. 141°C, sp. gr. 0.863)
m- xylene	66% (b. p. 139°C, sp. gr. 0.862)
p- xylene	20% (b. p. 136°C, sp. gr. 0.861)
ethylbenzene	4% (IL p. 136°C, sp. gr. 0.876)

Xylene obtained by cracking heavy petroleum hydrocarbons has approximately: 20-47% of *o*- and *p*- xylene, 30-45% of *m*- xylene, 12-25% of ethylbenzene and 8-10% aliphatic hydrocarbons.

The composition of the xylene obtained by distillation of Borneo petroleum is much the same as that of the xylene from coal.

Due to a relatively high content of the *m*- isomer xylene derived from coal or xylene from Borneo oil is the most convenient starting material for the preparation of nitration grade xylene.

Small differences in the boiling points of the xylene isomers make the preparation of pure *m*- xylene by distillation impossible. Nevertheless, boiling ranges of fractions suitable for nitration can be established.

Dobrianskii [19] tabulated the boiling points of the isomeric xylenes under various pressures (Table 91).

TABLE 91

BOILING POINTS OF ISOMERIC XYLENE

Pressure mm Hg	ortho	meta	para
740	143.50	137.90	137.20
750	144.00	138.40	137.70
755	144.25	138.65	137.95
760	144.50	138.90	138.20
765	144.75	139.15	138.45
770	145.00	139.40	138.70

According to Soviet data (Kravchinskii [3]), from the fraction of commercial xylene boiling below 136.5°C a nitration product of low value is obtained, melting at a low temperature owing to its high content of oily products. The fractions boiling in the range 136.5-140°C are much more convenient for nitration, since the product obtained has a melting point of 164.5-166°C.

Fractions boiling in the temperature range 140-141.5°C again yield a lower quality product containing a high proportion of oil.

Taking this into consideration, specifications (as in the U.S.S.R.) require a fairly narrow boiling range for xylene, for example, 95% of the product should distil between 136.5-140°C or 136.5-141.5°C.

The specific gravity of the xylene at 15°C should be 0.862±0.002. Only a slightly yellow colour (straw yellow) produced by treating xylene with sulphuric acid is permissible.

A low specific gravity of the fraction indicates a high content of *p*- xylene, while a high specific gravity indicates a high content of ethylbenzene. A low boiling point is an indication of high proportions of ethylbenzene and *p*- xylene in the xylene and a high boiling point indicates the presence of large amounts of *o*- xylene.

Since analytical results do not give a clear idea as to the usefulness of xylene for nitration, nitration tests on a laboratory scale are recommended.

Recent German specifications for nitration grade xylene require determination of the freezing point of *m*- xylene, which should not be lower than -52°C. 100% of the xylene should distil within 1-2°C.

Separation of the xylene isomers by freezing. Besides the distillation method for separating *m*- xylene a method of separating the isomers by fractional crystallization, with freezing out, is used. The method is based on differences in the freezing points of the isomers:

o- xylene	f. p. -27.1°C
m- xylene	f. p. -54.8°C
p- xylene	f. p. +13.2°C

Such big differences enable the *o*- and *p*- isomers to be separated readily from *m*- xylene.

A drawback of this method is that the mixture has to be cooled to a very low temperature, which is costly. Further, if very pure *m*- isomer is to be prepared, it should be crystallized out, which is a very expensive operation as it requires cooling to a temperature below -55°C.

Chemical method of separating *m*- xylene. The method is based on the different capacities of the isomers to undergo sulphonation, and on the different extent to which the sulphonic acids are hydrolysed. It has been shown that *o*- and *m*- xylene can be sulphonated with concentrated sulphuric acid under conditions which leave *p*- xylene unaffected. *m*- Xylenesulphonic acid can be hydrolysed to *m*- xylene at a temperature too low for the hydrolysis of *o*- xylenesulphonic acid.

In practice, the process is effected as follows. Crude *m*- xylene, containing 60-70% of *m*- xylene, is mixed with sulphuric acid (sp. gr. 1.84) whereupon the temperature rises to 45°C. Then the mixture is heated to 50°C and allowed to remain at this temperature for 2 hr. Under these conditions sulphonation of the *o*- and *m*- isomers takes place. The sulphonic acids may be separated from unconverted *p*- xylene either by extraction with water or by expelling the *p*- xylene by steam distillation.

The temperature of the aqueous solution of sulphonic acids is brought to 130°C. Hydrolysis of sulphonated *m*- xylene follows :

$$C_6H_3(CH_3)_2SO_3H + H_2O \rightarrow C_6H_4(CH_3)_2 + H_2SO_4 \qquad (3)$$

The sulpho derivative of *o*- xylene undergoes hydrolysis only at 160°C and it remains unaffected during the reaction. This permits the separation of *m*- xylene from an aqueous solution of sulphonic acid.

The *m*- xylene isolated in this way is of very high purity. When nitrated it yields a product having a melting point only slightly lower than that of chemically pure 2,4,6-trinitro-m-xylene.

One-stage preparation of TNX

The nitration of xylene to trinitroxylene may be carried out in one, two or three stages.

The one-stage nitration has the advantage of giving a higher yield of the nitro compound as compared with other methods. On the other hand it has also a drawback, as it requires larger quantities of acids. The one-stage method of nitration is recommended when the product must be obtained in a short time, and cost is of minor importance.

The method was used in Russia during the 1914-1918 War. It was worked out by Solonina [8] and applied in the Shterovka factory. As Kravchinskii [3] reported, the operation was carried out in the following way.

Nitrating mixture of a composition:

HNO_3	18-19%
H_2SO_4	78-79%
H_2O	3%

is run into the nitrator. Then the stirrer (120-150 r. p. m.) is started and cooling water is passed through the jacket and the coil of the nitrator. When the temperature reaches 12°C xylene is run into the nitrator at such a rate as to allow the whole quantity to be introduced in 4-4.5 hr (for 1 part by weight of xylene 13.5 parts of the nitrating mixture is applied). Thus, the excess of nitric acid used amounts to 43%). During the introducing of the xylene a temperature of 30-40°C is maintained, and by the end of the operation it is raised to 65-70°C.

When all the xylene has been run into the nitrator the temperature rises spontaneously to 90°C. This is a critical moment, as the rise of temperature is accompanied by vigorous oxidation and frothing of the reaction mixture, owing to the evolution of gases (mainly carbon dioxide and nitrogen oxides). The reaction mixture is likely to run over if the process is too vigorous. When the violent reaction has subsided the mixture is heated to 105°C, this temperature being maintained for one hour.

The whole operation takes nearly 7 hr, including half an hour for charging the nitrator, 6 hr for the nitration, and half an hour for unloading.

After nitration has been completed the mixture is sent to a settler and allowed to remain there for 2 hr for the nitro compound to settle. The product is separated from the spent acid on a vacuum filter, and then transferred by means of shovels or by a stream of water to a washing tank.

The composition of the spent acid is:

HNO_3	0.8-1.5%
NO_2	3-5%
H_2SO_4	81-82.5%
nitro compounds	3-4.5%
H_2O	8-11%

Trinitroxylene is washed in a lead-lined wooden tank (Fig. 103) first several limes with cold water (1 part of water for 1 part of the product), then with hot water (80-85°C) and finally with cold water again. In all, the washing is repeated 6-7 times, each washing taking about 1 hr.

Compressed air, introduced through a lead bubbler, is used for mixing the nitro compound with water.

When the acid content of the washings falls below 0.1%, the product together with the washing water is drained off to a centrifuge. At this stage the trinitroxylene still contains oily admixtures apart from water.

When heated, it melts partially at 120-125°C, and becomes completely molten at 160-177°C. The melting point of the main part of the product is 163°C.

By passing moist hot trinitroxylene through a centrifuge not only the water but also the oily components are removed. Under these circumstances the product

loses about 12% in weight. The oily product separated along with water is allowed to settle in special tanks and should then be utilized for special purposes. After centrifugation, the trinitroxylene still contains 15-18% of water. As Kravchinskii believed, the melting point of the product could be raised from 168°C to 176°C as a result of centrifugation.

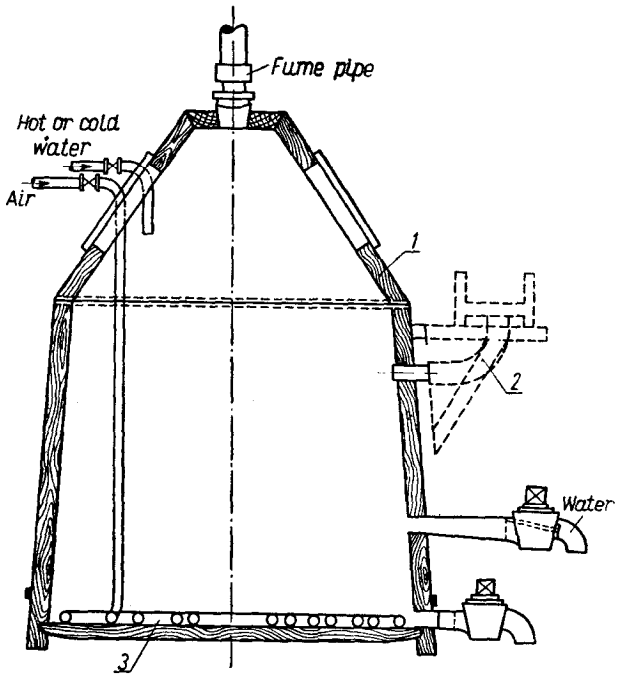


FIG. 103. Wooden vat for washing TNX: 1 - wooden lead lined walls, 2 - rubber sleeve to introduce TNX, 3 - lead bubbler (Kravchinskii [3]).

Two-stage preparation of TNX

The two-stage preparation of TNX consists in the nitration of *m*- xylene in two stages.

This method has been applied in the U.S.S.R, two modes being used:

Xylene -> DNX -> TNX

or Xylene -> MNX -> TNX

Nitration via DNX. In the first stage of the process - dinitration of xylene- the following nitrating mixture is used:

HNO_3	20%
H_2SO_4	65%
H_2O	15%

The mixture is run into the nitrator, and when it has attained a temperature of 25°C, feeding with xylene starts until the acid to xylene ratio is 6.5, which corresponds to an excess of HNO_3 amounting to 10% of theoretical. While adding

xylene a temperature of 35-40°C is maintained. Then it is gradually raised to 100°C, where it is maintained for 14 hr.

After cooling (while stirring) the dinitroxylene, which is partly crystalline and partly oily, is separated from the spent acid by centrifugation. The melting point of the product ranges from 37° to 61.5°C.

From 100 parts by weight of xylene 163.8 parts by weight of dinitroxylene are obtained, the yield being 94% of theory.

The composition of the spent acid is:

HNO_3	1.7%
H_2SO_4	74.3%
H_2O	24.0%

The wet product is separated into two fractions - liquid (oily) and solid. Usually 20% of liquid and 80% of solid dinitro-m-xylene is obtained.

For the second stage of the process, i.e. trinitration, the DNX liquid or solid obtained is charged into the nitrator and acid of a composition:

HNO_3	18%
H_2SO_4	60%
H_2O	2%

is added.

For 1 part of DNX 3.2 parts of the nitrating mixture are run in, thus the excess of HNO_3 is 80% of the calculated amount.

Temperatures during the operation are maintained as follows: 50-55°C during addition of the acid, then 110°C for an hour, and finally 120°C for two hours. When nitration is completed, TNX is separated from the spent acid on a vacuum filter, after cooling to 20°C.

The spent acid from the process has the following composition:

HNO_3	6%
H_2SO_4	86%
H_2O	8%

From 100 parts of DNX 105 parts of TNX are obtained, which makes 86% of the theoretical yield.

From liquid DNX solid grade II TNX (m. p. 164°C) and liquid TNX are both obtained.

From solid DNX grade I crystalline TNX (m. p. 177°C) is obtained.

100 kg of *m*- xylene yield the following quantities of TNX:

147-154	kg of the grade I product
25.6	kg of the grade II product
1.0	kg of the liquid product.

Nitration via MNX. The process worked out by Filippov [8a] consists of two stages: mononitration followed by trinitration.

For one part of *m*- xylene, 2.5 parts of nitrating mixture of the composition:

HNO_3	25%
H_2SO_4	59%
H_2O	16%

are added. Thus, the quantity of HNO_3 amounts to 105% of theoretical. The nitrating mixture is prepared from the spent acid from trinitration.

During the introduction of the nitrating mixture into the nitrator a temperature of 30-40°C is maintained. After all the acid has been introduced and the mixture in the reactor has been kept at 40-45°C for two hours, it is cooled to 15-20°C, the stirrer is stopped, and after 15-20 min the nitro compound formed is separated from the spent acid.

100 parts of *m*- xylene yield 130-140 parts of MNX, which corresponds to 91-98% of theory.

For the conversion of MNX to TNX a nitrating mixture of the composition:

HNO_3	17.5%
H_2SO_4	79.0%
H_2O	3.5%

is added at a temperature of 10-12°C, the proportion of the reagents being 6 parts of the nitrating mixture for 1 part of mononitroxylene. Such a proportion corresponds to an excess of HNO_3 of nearly 25%.

During the first hour of the nitration process the temperature rises gradually to 50-60°C and finally reaches 65°C. Then the temperature is raised gradually to 110-120°C, and maintained then for 1 or l½ hr. After cooling, the trinitroxylene is filtered off, washed with cold, and then with hot (80-90°C) water, and finally the wet, hot product is separated from oily substance by centrifugation.

Spent acid from trinitration has the composition:

HNO_3	2-6%
H_2SO_4	82-85%
H_2O	11-15%

From 100 parts of MNX 170-180 parts of TNX are obtained; thus the yield is 70-80% of the theoretical.

The melting point of TNX prepared in this way is 164-166°C.

Three-stage preparation of TNX†

Mononitration. For 100 parts of *m*- xylene, separated from its isomers by sulphonation, 220 parts of a nitrating mixture of the composition:

HNO_3	28%
H_2SO_4	56%
H_2O	16%

are used.

The nitrating mixture is prepared from spent acids from di- and tri-nitration, by fortifying them with fresh concentrated acids.

The nitration temperature should not exceed 35°C. From 100 parts of *m*- xylene, 130-135 parts of MNX are obtained, i.e. the yield is 90-94% of the theoretical. Further procedure (separation of the nitro compound from the spent acid) is similar to that used in other nitration processes.

† Soviet and French methods (according to Kravchinslcii [3] and Pascal [20] respectively).

Nitration of MNX **to DNX.** For 100 parts of MNX 140 parts of a nitrating mixture of the composition:

HNO_3	11%
H_2SO_4	74%
H_2O	15%

are used.

The mixture is prepared from the spent acid from trinitration by fortifying it with concentrated acids. During the mixing of mononitroxylene with the acid a temperature of 35-50°C is maintained. Then it is raised to 85°C and the reaction mixture is allowed to remain at this temperature for one hour. From 100 parts of mononitroxylene 137 parts of dinitroxylene are obtained, thus the yield is 95% of the theoretical.

Nitration of dinitroxylene to trinitroxylene. For 100 parts of dinitroxylene 230-300 parts of a nitrating mixture of the following composition are applied:

after Kravchiiskii [3]		after Pascal [20]	
HNO_3	10-15%	HNO_3	15-21%
H_2SO_4	76-81%	H_2SO_4	70-75%
H_2O	9-10%	H_2O	9-10%

The nitrating mixture is gradually run into dinitroxylene in the nitrator, at first at 60-70°C, and by the end of the procedure at 80-85°C. Then all is carefully heated to 95-100°C or 110-120°C.

When the reaction has been completed the nitrator contents are cooled and the product obtained is separated from the spent acid.

As Pascal [20] reported, from 100 parts of dinitroxylene 105 parts of trinitroxylene were obtained, the yield being 85% of the theoretical. In Table 92 the conditions and yields (calculated on toluene or xylene) obtained in the nitration of toluene and xylene are tabulated for comparison.

TABLE 92

COMPARISON OF NITRATION CONDITIONS FOR TOLUENE AND XYLENE (PASCAL [20])

	Product obtained					
	MNT	MNX	DNT	DNX	TNT	TNX
Composition of the nitrating mixture HNO_3	28	28	32	11	19	15-21
Composition of the nitrating mixture H_2SO_4	56	56	61	74	80	70-75
Composition of the nitrating mixture H_2O	16	16	7	15	0	9-10
Maximum temperature, °C	60	35	90	85	120	95-120
Yield, obtained	143	130-135	188	178-185	190	170
Yield, calculated	149	144	198	187	246	229
Yield ratio $\frac{\text{Xylene}}{\text{Toluene}}$	0.930		0.962		0.894	

Mononitration of xylene (I. G. Leverkasen method). To the nitrator containing I400 1. of spent acid from the previous nitration, 50 1. of xylene are added (thus the

xylene is partly nitrated by the residual nitric acid still present in the spent acid). Then over a period of 3-4 hr, 1950 kg of xylene and about 3000 kg of a nitrating mixture :

HNO_3	28%
H_2SO_4	56.5%
H_2O	15.5%

are run in, the initial temperature of 15°C rising to 35°C by the end of the procedure.

Then over half an hour the rest of the acid is introduced so that the total quantity of the fresh nitrating mixture amounts to 4150 kg. The mixture in the nitrator is then stirred for another half an hour and conveyed to a separator where it is allowed to remain at rest for 2 hr so as to separate the nitro compound from the spent acid.

Part of the spent acid, having an average composition:

HNO_3	0.3%
NO_2	0.4%
H_2SO_4	70%
H_2O	29%

is sent to a concentration plant, while the rest is recycled to the nitrator.

The nitroxylene is washed with water until free from acid (test with Congo paper), then it is mixed with 150 1. of 30% sodium hydroxide solution at 70°C. Thus any nitroxylenols resulting from oxidation are removed.

The nitroxylene is then mixed with 50 kg of sodium carbonate and steam is passed through the mixture to remove unnitrated volatile compounds. The sodium carbonate dissolves in water and the aqueous solution thus formed is separated from nitroxylene.

The nitroxylene is further washed, this time twice with a 2.5-3% solution of NaOH at a temperature of 60°C and finally with water until quite free from alkalis.

From 100 kg of xylene 125 kg of nitroxylene can be obtained, which is 88.5% of the theoretical yield.

Purification of TNX

If trinitro-m-xylene has been prepared from pure *m*- xylene simple washing with hot water is sufficient to obtain a product of high purity. Otherwise, the removal of oily components by hot centrifugation is necessary. Additional purification by washing the product in the centrifuge with organic solvents (alcohol, benzene) may be applied. In consequence of the higher solubility of nitro derivatives of *o*- and *p*- xylene, mainly these compounds are removed.

A sodium sulphite wash may also be applied. According to Kravchinskii [3], the agitation of trinitro-m-xylene with a 7-9% solution of sodium sulphite at 70°C for 4 hr results in the complete removal of oily products. However, losses caused by this process may be considerable (15-25%), so that this method of purification does not always pay.

Drying. The trinitro-m-xylene, purified as above, and containing 13-18%

of water, is dried in tunnel or chamber driers at 60-70°C, until the water content falls to 0.1%. This operation takes 12-24 hr, depending on the type of drier. The finished product is a crystalline, slightly yellow powder.

NITRO DERIVATIVES OF OTHER HOMOLOGUES OF BENZENE

NITRO DERIVATIVES OF MESITYLENE

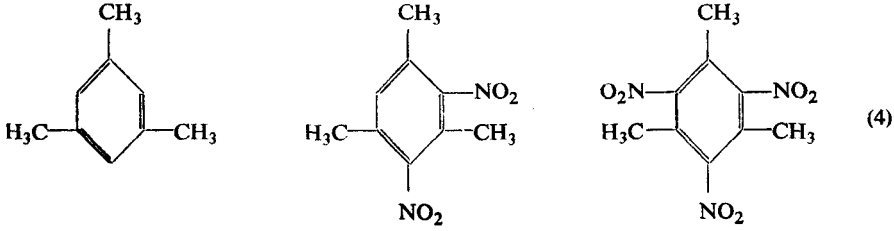
Trinitromesitylene is of some importance as an explosive due to the fact that the raw material - mesitylene - is easily obtainable by reacting acetone with sulphuric acid (Kane [21]).

However, as Tishchenko [22] reported, the yield of the reaction did not exceed 27% of the theoretical. Ipatiyev [23] found that mesitylene could be obtained in a yield up to 36% by reacting acetone with hydrogen chloride at a pressure of 100 atm.

Sucharda and H. Kuczynski [24] found that the yield could be increased to 47% by reacting the two compounds in sealed tubes at 145-195°C.

Cahours [25] obtained trinitromesitylene by treating mesitylene with a mixture of nitric and sulphuric acids. Repeating these experiments, A. W. Hofmann [26] obtained dinitromesitylene as well.

Nitration of mesitylene to di- and tri-nitromesitylenes proceeds with great ease :



(4)

m. p. 89°C m. p. 235°C

Dinitromesitylene can be obtained by dissolving mesitylene in fuming nitric acid, followed by the addition of water which causes dinitromesitylene to precipitate. For the preparation of trinitromesitylene by the Blanksma [7] method, mesitylene is dissolved in sulphuric acid (partial sulphonation taking place), and the solution is added to nitric acid (sp. gr. 1.52). Trinitromesitylene then precipitates, as white crystals, dissolved by organic solvents only with difficulty. Kholevo [26a] nitrated mesitylene with the nitrating mixture (27% HNO_3, 69% H_2SO_4, 4% H_2O) to yield trinitromesitylene.

The explosive power of trinitromesitylene is rather low - of the order of DNT. Its sensitiveness to impact, however, is relatively high - of the order of TNX -and much higher than that of DNT. This can be explained by the presence of the largest possible number of substituents on the ring.

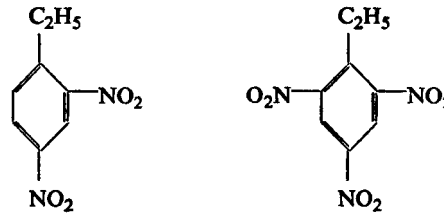
NITRO DERIVATIVES OF ETHYLBENZENE

Ethylbenzene is always present in crude xylene and in solvent-naphtha. Since the boiling point of ethylbenzene (136°C) is identical with the boiling point of *p*- xylene, the two are difficult to separate. It is possible to do so by cooling. as the freezing point of ethylbenzene is -94.9%.

Fittig and Tollens [27] obtained ethylbenzene by synthesis from chlorobenzene and ethyl chloride. At first they believed it was xylene (basing their view on its boiling point). However, the substance did not yield a crystalline product when nitrated, as in the case of xylene, but an oily one, from which they inferred that the "ethylphenyl" they had obtained was not xylene.

Beilstein and Kuhlberg [28], by nitrating ethylbenzene with a mixture of nitric and sulphuric acids at a low temperature obtained two oily products which proved to be *o*- and *p*- nitroethylbenzenes.

Weisweiller [29], and later Schultz and Sander [30] obtained 2,4-dinitroethylbenzene and 2,4,6-trinitroethylbenzene:



2,4-Dinitroethylbenzene (b. p. 167.5% at 13 mm Hg, m. p. +4°C) was obtained by reacting ethylbenzene with a mixture of 2 parts of sulphuric acid (sp. gr. 1.84) and 1 part of nitric acid (sp. gr. 1.43). After the reaction had subsided the temperature of the mixture was raised to 125-130°C and kept at this temperature for 10 min.

For the preparation of trinitroethylbenzene (m. p. 37°C) ethylbenzene was treated with a mixture of nitric acid (sp. gr. 1.525) and 30% oleum, initially at 0°C, then the temperature was raised to 100°C and maintained there for 15-20 min. After cooling, the trinitroethylbenzene formed remained in the solution. By pouring the latter into water, the oily product was separated, which then solidified to form a crystalline mass.

With naphthalene and aromatic amines (e.g. aniline) trinitroethylbenzene forms addition compounds.

The explosive power of trinitroethylbenzene is rather low, so the compound itself is of no value. However, it is one of the chief components of liquid nitro-solvent-naphtha, and is sometimes used as an ingredient in the preparation of explosive mixtures.

p- Nitroethylbenzene is obtained as an intermediate in chloramphenicol (chloromycetin) synthesis.

NITRO-SOLVENT-NAPHTHA

Difficulties met in separating chemical individuals from higher fractions of light oil and lower fractions of middle oil stimulated attempts at the direct nitration of solvent-naphtha, the name given to a mixture of isomers comprising xylenes, ethylbenzene, pseudo-cumene (1,2,4-trimethylbenzene), ethyltoluene and mesitylene.

The mixture is obtained as a fraction boiling within the range 120-175°C. lt should be nitrated with great care, since it reacts violently with nitric and sulphuric acids. Nitration techniques have been described in a number of patents (Dahmen [31]; Blechner, Lopez and Distler [32]; Schultz [33]):

In most of the descriptions temperatures of 25-30°C are quoted for the first nitration stage and 80°C towards the end of the process. The nitrating mixture is prepared from concentrated sulphuric (sp. gr. 1.84) and nitric (sp. gr. 1.50) acids.

The product is a mixture of oil with a solid substance, the quantity of the latter depending on the fraction of solvent-naphtha used.

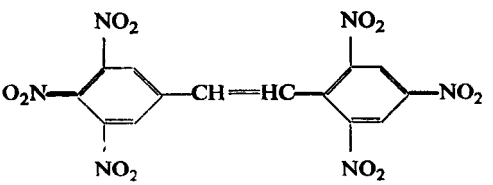
Thus, Blechner, Lopez and Distler [32] give the following data on the nitration of various solvent-naphtha fractions (Table 93).

TABLE 93

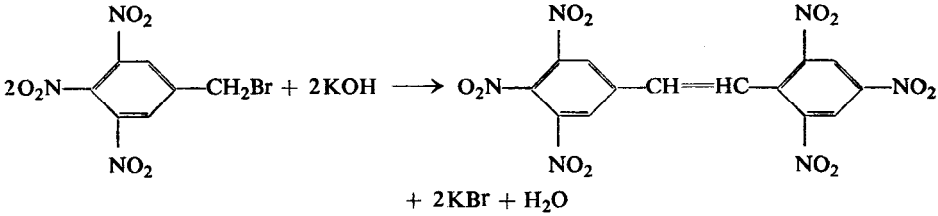
Fraction boiling within the temperature range, °C	Average yield	
	solid substance, %	oily substance, %
140-145	80	20
150-155	40	60
160-165	100	-

For some time nitro-solvent-naphtha was a widely used component of explosive compositions. Liquid fractions of the nitrated substance have also been used in the manufacture of mining explosives and even of smokeless powder, as an explosive solvent for nitrocellulose. In the latter case liquid nitro-solvent-naphtha acted as a substitute for part of the nitroglycerine. This type of smokeless powder was also manufactured in Poland in the period between the two World Wars (Kardaszewicz, Markiewicz and Smisniewicz [34]).

HEXANITROSTILBENE



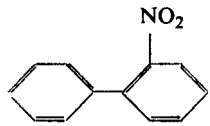
Pure hexanitrostilbene (m. p. 211°C, with decomposition) was obtained by S. Reich, Wetter and Widmer [35] by treating boiling trinitrobenzyl bromide with alcoholic potassium hydroxide:



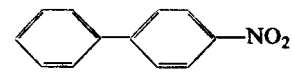
(5)

NITRO DERIVATIVES OF DIPHENYL

Diphenyl is nitrated with nitric acid in the presence of acetic acid to form a mixture of mononitro derivatives:

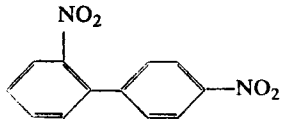


2-Nitrodiphenyl
m. p. 37°C

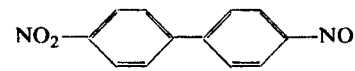


4-Nitrodiphenyl
m. p. 114°C

By boiling with nitric acid (98%) or with a mixture of nitric (77%) and sulphuric acids, diphenyl yields a mixture of 2,4'- and 4,4'-dinitrodiphenyl:

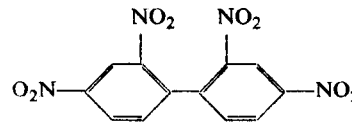


m. p. 93-94°C



m. p. 233°C

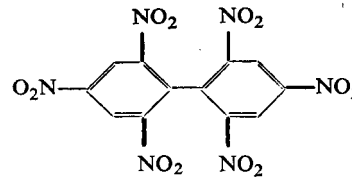
By direct nitration no more than four nitro groups can be introduced into diphenyl, 2,4,2',4'-tetranitrodiphenyl being formed (Losanitsch [36]; Ulhnann and Bielecki [37]).



m. p. 163°C

Nowadays the compound is not used in the explosives industry since its explosive power is only slightly higher than that of dinitrobenzene, while on the other hand its melting point is too high, and diphenyl, the raw material for its manufacture, is available only in small quantities.

Its hexanitro derivative: 2,4,6,2',4',6'-hexanitrodiphenyl



m. p. 238°C

has evoked much more interest as an explosive.

The compound may be obtained by Ullmann and Bielecki's [37] method, which consists in heating picryl chloride with copper powder in a high boiling solvent like nitrobenzene, toluene or xylene.

Its explosive power is higher than that of hexanitro-diphenylamine (hexyl) by nearly 10%. According to a patent granted to Sprengstoff A. G. Carbonit [38] the lead block test figure for the product is about 360 cm^3. The initiation temperature of the explosive is high - over 320°C. It has also the advantage of being only slightly toxic (less than hexyl). On the other hand its application is limited by the cost of manufacture, which requires picryl chloride. Because of its high melting point it cannot be used in the molten state. So it should either be compressed or used as an additive in fusible mixtures with other nitro compounds.

NITRATION OF MIXTURES

During World War II a method of preparing mixtures of nitro compounds (e.g. TNT and TNX, or TNT and tetryl, see Vol. IV) was developed by the Germans. It consisted in the nitration of the corresponding lower nitrated compounds, namely a mixture of mononitrotoluenes plus mononitroxylenes was nitrated in two stages to form trinitro compounds. In this way a product containing 20% of TNX and 80% of TNT was obtained.

A mixture consisting of 45 parts of TNX and 50 parts of tetryl was prepared by mixing mononitroxylenes and dinitromethylaniline in suitable proportions and nitrating them. To the nitration product TNT was added in such a quantity as to obtain a mixture composed of 45% of trinitroxylene, 50% of tetryl and 5% of TNT. The mixture melts at 80°C; it does not need washing with a sodium bicarbonate solution, as is the case with TNT. A simple washing with hot water will suffice. The mixture has proved to be a fully adequate substitute for TNT.

NITRO DERIVATIVES OF POLYMERS

During World War II a large amount of research was carried out in seeking fully synthetic polymeric materials which could substitute a semi-synthetic polymer such as nitrocellulose. This research was connected with the immense development of plastics chemistry, which began shortly before World War II and is still advancing at a great pace.

NITROPOLYSTYRENE

Investigations on the nitration of polystyrene go back to 1845, to the experiments of Blyth and Hofmann [39], who reacted boiling nitric acid with glassy polystyrene, which was obtained from styrene of natural origin, namely from Styrax resin. The product prepared contained 10.6% of N.

During World War II several authors resumed the investigations. G. B. Bachman and his co-workers [40] nitrated polystyrene with nitric acid (sp. gr. 1.50) and obtained products of various degrees of nitration depending on the nitration temperature: at 50°C a product containing 10.0% of N was obtained, while at 150°C the product contained 11.2% of N.

A vast amount of research was carried out by Zenftman [41], who proved the action of a nitrating acid on polystyrene to be limited to the nitration of the superficial layer of polymer granules only. The inside of the granules remained unaffected. A necessary condition for obtaining complete nitration of the substance is to use a nitrating mixture which completely dissolves the polymer. According to Zenftman, nitrating mixtures of a composition ranging from the anhydrous one:

HNO_3	70%	I
H_2SO_4	30%	

to that containing water:

HNO_3	76%	II
H_2SO_4	12%	
H_2O	12%	

are good solvents for polystyrene.

With a mixture of type I, a product containing up to 14.4% of N can be obtained, while a mixture of type II gives a product with about 9.4% of N.

The nitration of polystyrene is carried out in the following way. To a mixture containing

HNO_3	73%
H_2SO_4	26.5%
H_2O	0.5%

finely ground polystyrene is added, a temperature of 18°C being maintained by cooling. The polystyrene to acid ratio is 1:20. After all the polymer has been added, the temperature is allowed to rise to 20°C. After one hour's stirring the polymer becomes completely dissolved in acid. After 4 hr from the beginning of the nitration process the solution is poured into water. Nitropolystyrene is then precipitated in the form of threads, which are washed with water, ground in a ball drum and again washed with hot water (90-95°C). From 100 g of polystyrene nearly 33 g of the nitrated product containing 13.4% of N can be obtained.

It has been shown by analysis that even under the most severe conditions of nitration only two nitro groups can be introduced into the benzene ring. The oxidation of nitropolystyrene to the corresponding nitrobenzoic acid (with MnO_2 in sulphuric acid) has shown, according to Zenftman [41], that the substitution

occurs in the 4- and 2,4-positions of the benzene ring. Hence one can infer that during the nitration of polystyrene the first nitro groups take the position para to the vinyl group and then part of the rings undergoes further nitration, the next nitro groups taking the ortho position.

During the nitration, polystyrene undergoes partial degradation to an extent which depends on the nitration conditions and is greatest at the beginning of the reaction.

Nitropolystyrene is soluble in 90% nitric acid, nitroglycerine, nitrobenzene and cyclohexanone. It burns without melting. Zenftman and MacLean [42] suggested taking advantage of this by using the product as a combustible binder for explosive mixtures instead of nitrocellulose.

Médard [43] has examined the explosive properties of nitropolystyrene containing 13.9% of N, i.e. consisting of about 90% of the dinitro and 10% of the mononitro compound. In his investigations he compared nitropolystyrene with dinitrotoluene and found the former to be a less powerful explosive and less sensitive to impact.

The rate of detonation of nitropolystyrene of density 0.25 in a steel pipe 36-42 mm in diameter is only 1510 m/sec.

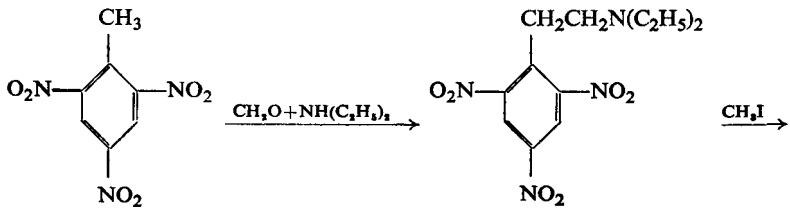
The density of nitropolystyrene is very low, due to its "fluffiness". Médard suggested its use in the manufacture of ammonium nitrate mining explosives of low density, hence of a relatively low power. The following figures give some idea of such mixtures:

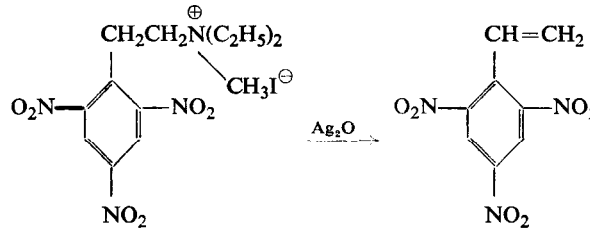
Nitropolystyrene	15%	12.75%
Ammonium nitrate	85%	72.75%
Sodium chloride	-	15%
Density	0.6	0.72
Lead block expansion test (picric acid = 100)		120
Rate of detonation	-	2720 m/sec

Attempts to prepare nitropolystyrene by the nitration of styrene followed by polymerization of the nitro derivatives, have failed.

Although it was possible to obtain the monomer 2,4,6-trinitrostyrene (Wiley and Behr [44]) every attempt to polymerize it has proved useless. This is understandable in the light of the fact that aromatic nitro compounds inhibit polymerization processes (p. 214). Similarly 2,4-dinitrostyrene has not been polymerized.

2,4,6-Trinitrostyrene has been prepared by these authors from trinitrotoluene in the following series of reactions:

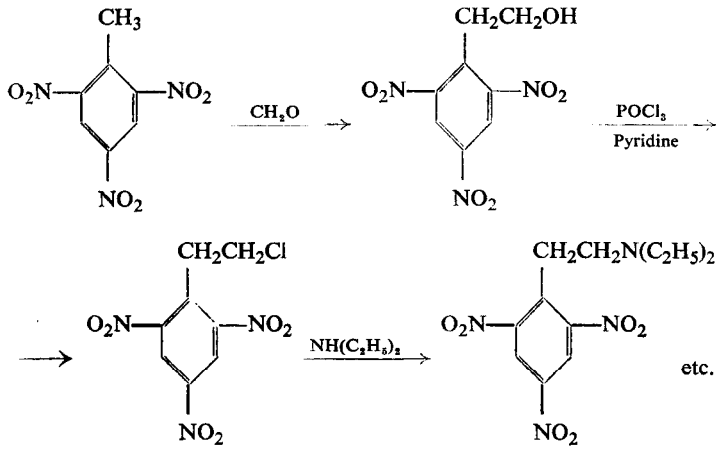




(6)

m. p. 65°C

Bonecki and T. Urbanski [45] prepared the same substance, also from 2,4,6-trinitrotoluene, but in a different way:



(7)

The next steps were analogous to those mentioned earlier. High purity trinitrostyrene was formed with m. p. 140°C.

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CHAPTER XI

NITRO DERIVATIVES OF NAPHTHALENE

GENERAL INFORMATION

NAPHTHALENE is easier to nitrate than benzene, and one or two nitro groups can be readily introduced into it. The first group enters the α– position, the second takes the α– position on the ring having no substituents. An isomer with a nitro group in position 3 to the first one, on the same ring, is also formed in an insignficant quantity. The introduction of the third nitro group leads to the formation of several isomers.

Armstrong and Wynne [1] have established an empirical rule :

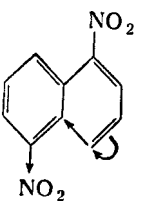
(a) a further group will not enter a position contiguous to a nitro group;

(b) a further group, other factors being equal, will tend to enter the nucleus at a position *peri* to an α– nitro group.

Under drastic conditions of nitration a further nitro group can be introduced into a naphthalene molecule.

By analogy with the rules of substitution in benzene based on the resonance theory and by considering that the quinonoid positions in naphthalene relative to 1 and 2 are 2,4,5,7 and 1,6,8 respectively a less empirical rule of substitution can be established.

Donaldson [2] gives an example. In 1,8-dinitronaphthalene the 3- and 6-positions are the least deactivated and nitration leads to 1,3,6,8-tetranitronaphthalene. Where two positions remain open the α– position shows a greater activity because of the nature of the naphthalene ring. An anomalous and important case is that of 1,5 dinitronaphthalene, in which only positions 3 and 7 are not deactivated. The main product of nitration of 1,5-dinitronaphthalene is 1,4,5-trinitronaphthalene and not 1,3,5- as would be expected. This led Hodgson and Ward [3] to conclude that the predominant hybrid in 1,5-dinitronaphthalene is



It favours electrophilic substitution in position 4. Modern approach to substitution rule consist in molecular orbital calculations [45].

Derivatives with β– nitro groups are more readily nitrated than the others. This Hodgson attributed to a higher electronegativity of β– nitro groups, particularly in the presence of vacant α– positions which are easy to substitute.

Hodgson has summarized the results of the nitration of dinitronaphthalenes (Table 94).

TABLE 94

starting material	Trinitro derivatives	Tetranitro derivatives
1,3-	1,3,8-	1,3,6,8-
1,4-	1,4,5-	1,3,5,8- and 1,4,5,8-
1,5-	1,4,5- and 1,3,5-	1,3,5,8- and 1,4,5,8-
1,6-	1,3,8-	1,3,6,8-
1,8-	1,3,8-	1,3,6,8-
2,6-	none	1,3,5,7-
2,7-	1,3,6-	1,3,6,8-

On reduction, acid reducing agents attack the α– nitro group preferentially, while sodium and ammonium sulphides reduce the β– nitro group.

Until the end of World War I and some years after, nitro derivatives of naphthalene were fairly widely used in mixtures with other explosives, for example with ammonium nitrate (e.g. Schneiderite) or with various other nitro compounds such as picric acid, as well as with potassium chlorate (cheddit) (Vol. III).

During World War II these compositions did not play any significant role. Used mostly in France, they dropped out of use from 1940 onwards.

At present nitronaphthalenes are scarcely used in the manufacture of explosives, mainly because of the shortage of naphthalene. The latter is used in large quantities in the manufacture of phthalic acid and of valuable dye intermediates. The large demand for phthalic acid and the lack of adequate supplies of naphthalene for its production have led to extensive research into the isolation of *o*- xylene and its oxidation to phthalic acid.

Nitronaphthalene is not an explosive. Dinitronaphthalene shows weak explosive properties and only trinitronaphthalene may be regarded as a true explosive. Tetranitronaphthalene is about as powerful an explosive as TNT (Lenze [4]).

Nitro derivatives of naphthalene have the advantage of being only slightly toxic. Although the output of nitro derivatives of naphthalene in Germany was high during World War I, no cases of poisoning were observed. However, eye irritation on exposure to the vapour or on contact with solutions of α– nitronaphthalene have been reported. The irritation is accompanied by eye-sight trouble (Frank [5]; Hanke [6]; Silex [7]; Caspar [8]).

Nitration of naphthalene was first mentioned in description of experiments by Laurent [9] between 1835 and 1842. On boiling naphthalene with nitric acid he obtained a mixture of mono-, di- and tri-nitronaphthalenes.

Later chemical investigations were aimed at establishing the conditions under which individual nitronaphthalenes could be formed. From the numerous investigations on the subject some of the more important work will be mentioned below.

Piria [10], by reacting naphthalene with nitric acid at room temperature for 5-6 days obtained mononitronaphthalene.

Roussin [11] prepared a mixture of mono- and di-nitronaphthalenes which he was able to separate by utilizing the fact that the latter is not soluble in carbon disulphide.

Troost [12] obtained nitro- and dinitro-naphthalenes by successive nitration of naphthalene. Darmstädter and Wichelhaus [13] found that the dinitronaphthalene thus obtained was a mixture of the two isomers.

More detailed studies had been carried out by d'Aguiar [14] who checked the results previously found. He isolated the following naphthalene derivatives :

two dinitronaphthalenes α and β (see p. 427)
three trinitronaphthalenes α,β and so called δ (see p. 431)
and two tetranitronaphthalenes α and β (see p. 434)

Beilstein and Kuhlberg [15] and Beilstein and Kurbatov [16] reinvestigated the methods of preparation and properties of dinitro derivatives of naphthalene and obtained a new product, γ– trinitronaphthalene.

The constitution of α–, γ– and δ– trinitronaphthalenes as well as of β–, δ– and γ– tetranitronaphthalenes has been determined by Will [17]. Friedländer [18] extended these investigations on β– trinitronaphthalene.

However, Dimroth and Ruck [18a] found that some of Will's data required correction: 1,2,5-trinitronaphthalene (δ according to Will's annotation) does not exist and δ– tetranitronaphthalene possesses the structure 1,4,5,8- and not 1,2,5,8,- as Will suggested.

The conditions under which mono-, di-, tri- and tetra-nitronaphthalenes are formed were investigated in detail by Patart [19] in extensive experimental work. By applying similar conditions (temperature and time) for the nitration of naphthalene with various nitrating mixtures, Patart determined the compositions of the products (the number of nitro groups) from the pressures they produced in a manometric bomb. The pressures, produced by pure substances were known, viz. :

nitronaphthalene (MNN) 927 kg/cm^2
dinitronaphthalene (DNN) 2296 kg/cm^2
trinitronaphthalene (TNN) 3280 kg/cm^2
tetranitronaphthalene (TetraNN) 3793 kg/cm^2

Similar experiments were carried out with the products of nitration of dinitronaphthalene.

Later Sapozhnikov [20] used Patart's data [19] for his triangular diagram, representing nitration of naphthalene (Figs. 104). In Fig. 105 and 106 the nitration curves for naphthalene and dinitronaphthalene are shown (Pascal [21]).

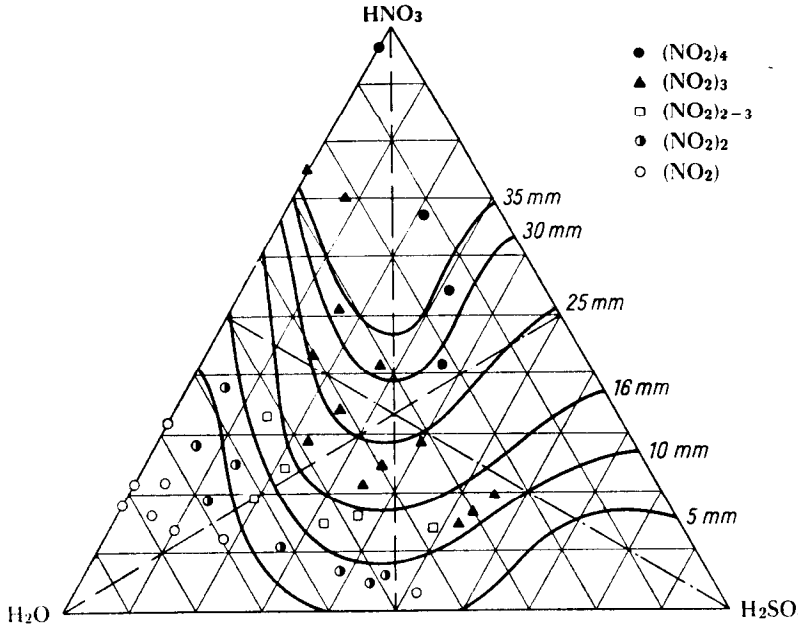


FIG. 104. Sapozhnikov's diagram of the nitration of naphthalene, according to Patart's experiments [21].

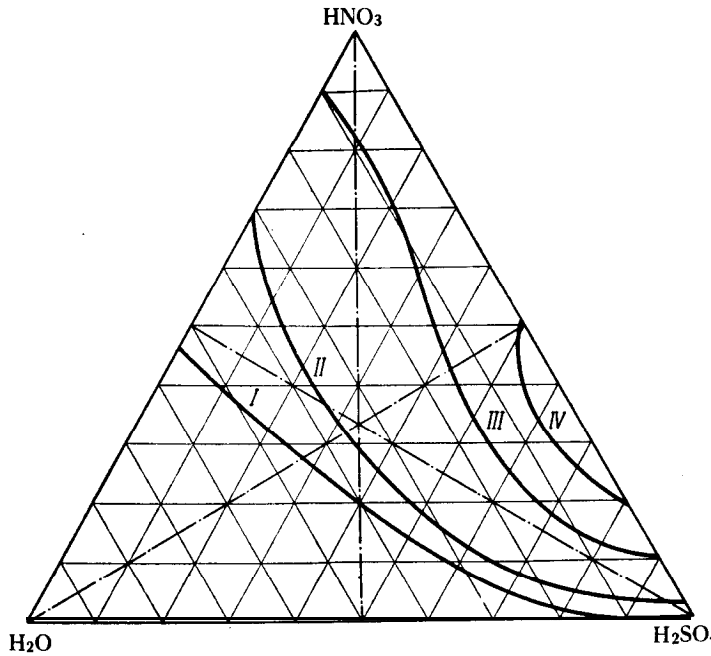


FIG. 105. Pascal's diagram of the nitration naphthalene-limits of formation: I - MNN, II - DNN, III - TNN, IV - TetraNN [20a].

Experiments on the nitration of naphthalene with nitrogen dioxide were carried out by Leeds [22] and more recently by Topchiyev [23]. The latter, in his experiments under various nitration conditions, obtained different products. At room temperature

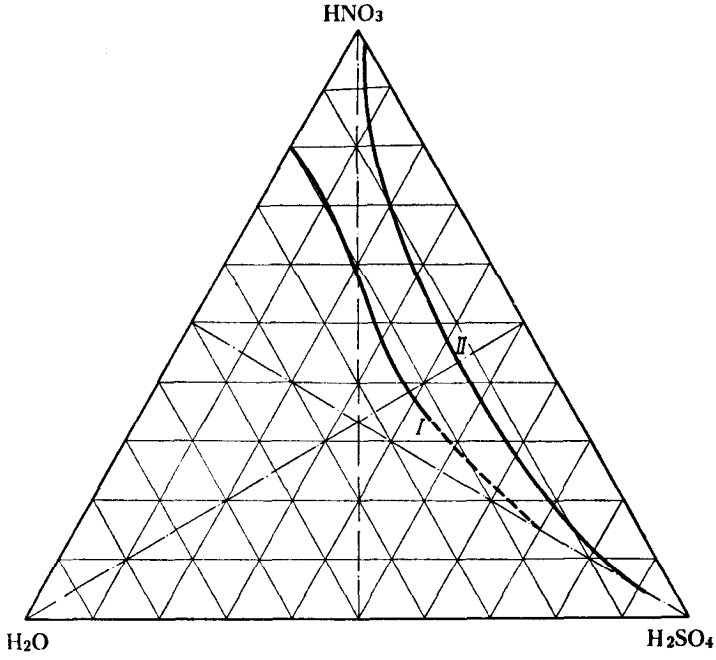


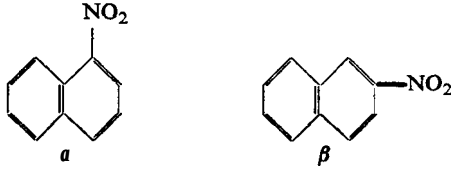
FIG. 106. Pascal's diagram of the nitration dinitronaphthalene-limits of formation: I - TNN, II - TetraNN [20a].

and with an excess of nitrogen dioxide, α– nitronaphthalene was obtained in a yield amounting to 96%; at 60°C, 1,5-dinitronaphthalene was formed (12% yield), along with α– nitronaphthalene (80% yield). At 150°C, in addition to these (in 30% and 36% yields) 1,8-dinitronaphthalene and a certain amount of 1,3,8-trinitronaphthalene were obtained (18% and 2% yields respectively).

Lantz [23a] has studied the nitration of naphthalene sulphonic acids (mono-, di- and tri-sulphonic acids). He stated that no displacement of the sulphonic groups with nitro groups occurs. By using nitrating concentrated mixtures he was able to introduce nitro groups so that the number of both SO_3H and NO_2 groups reached a maximum of four.

MONONITRO DERIVATIVES OF NAPHTHALENE

Both the mononitro isomers, α and β, are known:



α– Nitronaphthalene (m. p. 60-61°C; b. p. 304°C), MN or MNN, forms pale yellow needles, having the specific smell of a nitro compound. It is insoluble in water, but readily dissolved by most organic solvents.

α– Nitronaphthalene yields molecular compounds with picric acid, trinitrotoluene, nitromannite (described in the chapters dealing with these explosives).

When directly nitrated, naphthalene gives α– nitronaphthalene possibly with some traces of β– nitronaphthalene.

β– Nitronaphthalene (m. p. 79°C) can only be obtained by an indirect route from β– naphthylamine, and hence it has not found any practical use.

According to Patart, α– nitronaphthalene is formed as the result of nitrating naphthalene with a mixture of a composition within the range:

HNO_3	30-50%
H_2SO_4	0-30%
H_2O	40-50%

As Pascal's [20] investigations have shown, α– nitronaphthalene forms with naphthalene a eutectic melting at 36.7°C. The eutectic contains 26.5% of naphthalene. During the first stage of nitration, therefore, when both naphthalene and α– nitronaphthalene are present in the nitrator, a temperature of over 36.7°C should be maintained (e.g. 40-50°C) so as to keep the substance being nitrated in a molten state.

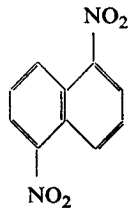
To this end some nitration methods recommend introducing into the nitrator a certain quantity of nitronaphthalene from the previous batch before the process begins.

After most of the naphthalene has been nitrated, the temperature in the nitrator shall be raised to 55-60°C to keep the nitration product molten, which will greatly facilitate the nitration.

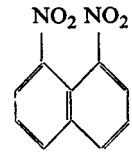
α– Nitronaphthalene is used as a component of explosive mixtures, as for example with picric acid for filling shells, and also in explosives used in mines and in chlorate explosives (Vol. III).

DINITRO DERIVATIVES OF NAPHTHALENE

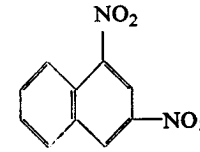
There are three isomeric dinitronaphthalenes, derivatives of α– nitronaphthalene. α– (1,5), β– (1,8), and γ– (1,3)-isomers known:



α
m. p. 215-216°C



β
m. p. 170-172°C



γ
m. p. 144°C

PHYSICAL PROPERTIES

They are fine grey-yellowish (sand-coloured) crystals. The colour of the commercial product frequently depends on its purity. The reddish colour met sometimes is evidence that nitrogen dioxide is present, absorbed by the product.

All the isomers mentioned are sparingly soluble in alcohol and ether. They dissolve more easily in benzene, toluene, acetic acid, acetone and turpentine.

The solubilities of both isomers of dinitronaphthalene, collected from the data of various authors are given in Table 95 (after Orlova [20b].

TABLE 95

SOLUBILITY OF DINITRONAPHTHALENES

Solvent	Temperature °C	Solubility, %	
		l,8-dinitro-napthalene	1,5-dinitro-naphthalene
Ethanol (anhydrous)	22	0.37	0.16
Ethanol 95%	19	0.06	0.06
Acetone	19	6.59	0.59
	boiling point	15.98	2.3
Acetic acid	boiling point	2.01	0.43
Chloroform	19	1.37	2.01
Dichloroethane	19	2.08	0.45
Benzene	50	0.06	0.02
Water	boiling point	0.07	insoluble

The commercial product obtained by the nitration of α– nitronaphthalene is a mixture of the 1,5- and 1,8- isomers, with only a small content of the 1,3-isomer. The melting point of the product ranges from 140-160°C. It is used for the preparation of explosives or for further nitration, without separating the isomers. The

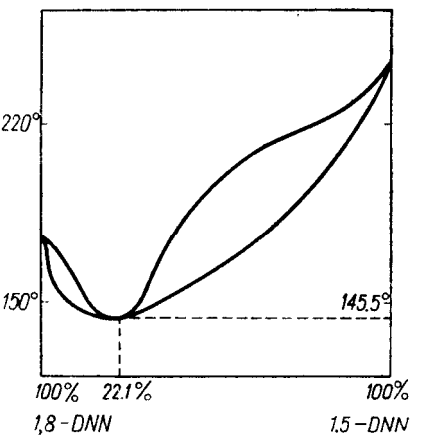


FIG. 107. System of 1,5- and l,8-dinitronaphthalenes (Pascal [20]).

1,5 and 1,8-isomers are separated only when they are to be used for the manufacture of dyestuffs intermediates. The separation is performed by means of selective solvents, as for example dichloroethane, which dissolves, the l,8-isomer more readily than the 1,5-isomer. Analytically, 1,5-dinitronaphthalene can be separated from the 1,8-isomer by paper chromatography (Franc [24]). The mobile phase consists of ethyl alcohol, water and acetic acid.

According to Pascal [20], both isomers form solid solutions belonging to Rooze boom's system III. When the content of the 1,5-isomer is 22.1%, they have the lowest melting point, which is 145.5°C (Fig. 107). The other systems examined by thermal analysis arc tabulated (Table 96).

TABLE 96

EUTECTICS WITH DINITRONAPHTHALENE : 1,5-DINITRONAPHTHALENE

The other component	% of DNN by weight	m.p. °C	Author
α– Nitronaphthalene	8	54.5	Pascal [21]
Picric acid	10	113.6	T. Urbanski and Kwiatkowski [25]
1,3,5-Trinitronaphthalene	10	101	Pascal [21]
1,3,8-Trinitronaphthalene*	27	165	Pascal [21]
	1,8-DINITRONAPTHALENE		
α– Nitronaphthalene	6	44	Pascal [21]
Picric acid	43	93	T. Urbanski and Kwiatkowski [25]
1,3,5-Trinitronaphthalene	22	88	Pascal [21]
1,3,8-Trinitronaphthalene*	52	135	Pascal [21]

* Minimum of Roozeboom system III.

COMPOSITION OF THE COMMERCIAL PRODUCT

Patart [19] found that commercial grade dinitronaphthalene, being a mixture of isomers, could be obtained by the nitration of naphthalene or α– nitronaphthalene with a mixture of the composition:

HNO_3	8-70%
H_2SO_4	0-76%
H_2O	16-30%

As numerous experiments have shown, the weight ratio of the isomers depends to a large extent on the nitration temperature.

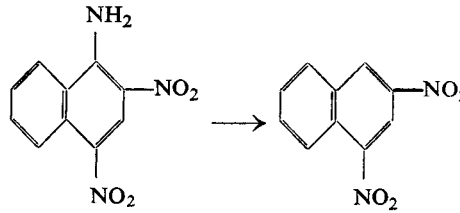
According to Pascal [20], at 70°C a mixture of 60% of the 1,8-isomer and 40% of the 1,5-isomer is formed. Hodgson and Whitehurst [26] have established the 1,5- to 1,8-isomers ratio to be nearly ½, when naphthalene is nitrated at 0-35°C.

Ward and Hawkins [27] nitrated 1-nitronaphthalene with a mixture of nitric (sp. gr. 1.42) and sulphuric (sp. gr. 1.84) acids, at a volume ratio 4:1 at 0°C and obtained a mixture of 1,8- and 1,5-dinitronaphthalenes, their ratio being about 70:30. 2-Nitronaphthalene, nitrated under similar conditions, gave a mixture of 1,6- and 1,7-dinitronaphthalenes along with 1,3,8-trinitronaphthalene, at a ratio of about 42:52:9.

According to Pictet [28] at very low temperatures ranging from -50°C to -60°C, nitration with a mixture of nitric and sulphuric acids resulted in the formation of a large quantity (about 46%) of the 1,3-isomer.

According to German sources (I. G. Ludwigshafen), commercial dinitronaphthalene consists of the 1,5-isomer (20%), 1,8-isomer (53%), the rest (27%) being a resinous substance.

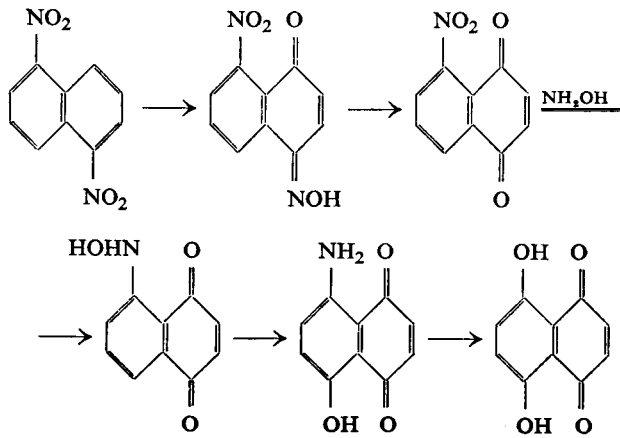
The 1,3-isomer has been obtained from 2,4-dinitro-a-naphthylamine, the amino group being removed by the conventional method, after diazotization (Liebermann [29]):



(1)

CHEMICAL PROPERTIES

It was known for long time that the 1,5- and 1,8-dinitronaphthalenes react under the action of concentrated sulphuric acid to yield naphthazarine - a valuable compound for dyeing [30]. The mechanism of the formation of this compound (based on experiments of Dimroth and Ruck [18a]) probably consists in the transformation of the nitro compounds to quinone-oximes and the reduction of one of the nitro groups by hydroxylamine split off the oxime:



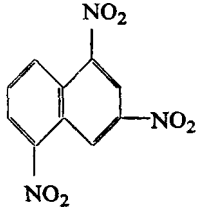
(2)

Gorst and Khlebnikov [31] reported that the colour of the solution of dinitronaphthalene in 84.5% H_2SO_4 did not change appreciably when kept at room temperature. When the concentration of sulphuric acid was 98% the solution darkened after 24 hr. Darkening occurs even more quickly when the sulphuric acid concentration is higher. The darkening is probably due to reactions similar to (2).

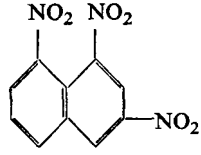
Application. A mixture of the dinitronaphthalene isomers is used in explosive compositions with picric acid and ammonium nitrate for military and mining explosives (Vol. III). The mixture is often referred to as "Dinal". It is also designated by the symbols DN or DNN. It is an explosive very difficult to detonate. The highest rate of detonation of Dinal, when using a very powerful detonator, is about 5100 m/sec (Calvet [32]).

TRINITRO DERIVATIVES OF NAPHTHALENE

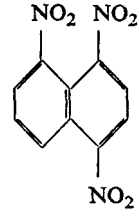
There are three isomers of trinitronaphthalene known, which can be obtained by direct nitration of a-nitronaphthalene, viz. : the α– (1,3,5-), β– (1,3,8-), and γ– (1,4,8-) or 1,4,5-isomers. The δ– isomer (1,2,5-) does not exist, according to Dimroth and Ruck [18a]. It is probably a mixture of the isomers.



α
m. p. 123°C
(119.5°C [18a])



β
m. p. 218°C



γ
m. p. 147°C

They are very fine crystalline, light brownish-grey products, sparingly soluble in organic solvents.

The crude product of the nitration of naphthalene or α– nitro- or commercial dinitro-naphthalene is a mixture of the four isomers. It melts at 115-160°C, the melting point depending on the nitration conditions.

Separation of the isomers can be achieved by taking advantage of their different solubility in alcohol. Thus, the 1,3,5-isomer dissolves in alcohol only with great difficulty. The 1,4,8-isomer does not dissolve in 70% alcohol, while the 1,3,8-isomer dissolves in the hot solution and may be precipitated from the solution either by cooling or by dilution (Pascal and Garnier [33]).

The conversion of dinitro- into trinitro-naphthalene may be achieved by using nitrating mixtures of varying compositions :

HNO_3	15-100%
H_2SO_4	0-70%
H_2O	0-15%

As Pascal [20] found, in the nitration of 1,5-dinitronaphthalene a product of the following percentage of isomers can be obtained:

1,3,5-	24.2%
1,4,8-	8.8%
1,2,5- (?)	47.5%

The rest (19.5%) consists of resinous products difficult to identify, plus unchanged dinitronaphthalene.

Using lower nitration temperatures (e.g. 65°C) results in a decrease of the y-isomer content. The contents of isomers in the product are then:

1,3,5-	34.4%
1,2,5- (?)	58.9%

Resinous substances are present in 6.7%.

According to Pascal, by the nitration of 1,8-dinitroniphthalene two isomers:

1,3,8-	85.1%
1,4,8-	9.6%

may be obtained, along with amorphous products and unconverted dinitronaphthalene.

Pascal also obtained, by nitrating naphthalene to trinitronaphthalene, a mixture of isomers of the composition:

1,3,5-	11-14.7%	1,4,8-	6-10%
1,3,8-	54.3-57.6%	1,2,5- (?)	21.5-25.5x

Patart reports that trinitronaphthalene can be prepared from naphthalene (1 part) using nitration mixtures (30 parts) of the composition:

HNO_3	18-100%
H_2SO_4	0-76%
H_2O	0-6%

When starting from dinitronaphthalene mixtures :

HNO_3	15-100%
H_2SO_4	0- 70%
H_2O	0- 15%

should be used for the preparation of trinitronaphthalene.

CHEMICAL PROPERTIES OF TRINITRONAPHTHALENE ISOMERS

1,3,5- (α)– and 1,3,8- (β)– trinitronaphthalenes form the following molecular compounds $\alpha_3.\beta$, $a.b$, $a.b_3$ (Pascal [20]).

Trinitronaphthalenes can be oxidized relatively easily to form corresponding nitrophthalic acids.

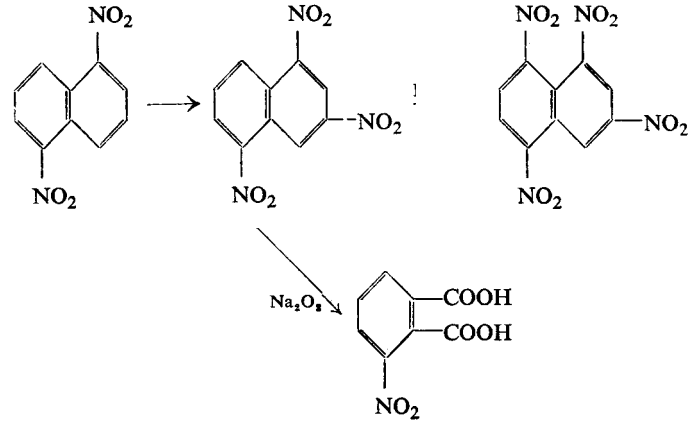
Some of the nitro groups can be relatively readily substituted by a methoxy or ethoxy group when heated with the corresponding sodium alcoholate. The oxidation of such a compound leads in the first place to rupture of the ring with the alkoxy group.

Oxidation reactions have been utilized for determining the constitution of trinitronaphthalene isomers.

STRUCTURE OF α– AND γ– ISOMERS

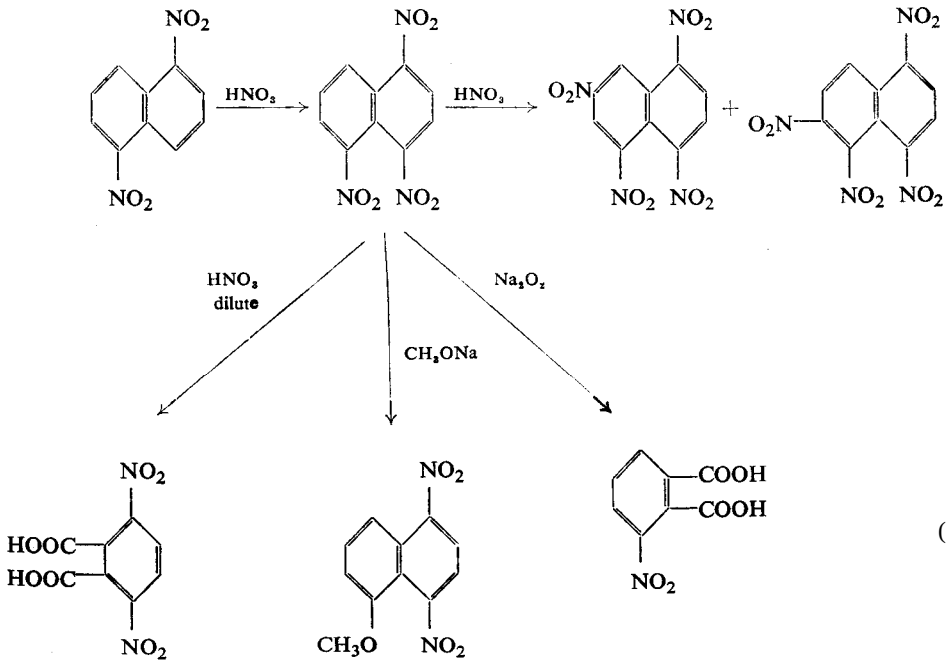
a - Trinitronaphthalene. Will [17] determined the constitution of this compound from the following reactions:

α– Trinitronaphthalene can be formed by the nitration of 1,5-dinitronaphthalene. When oxidized it yields *o*- nitrophthalic acid. Further nitration leads to 1,3,5-tetra-nitronaphthalene :



(3a)

g - Trinitronaphthalene. The constitution of this isomer has been determined from the reactions:



(4)

EXPLOSIVE PROPERTIES AND APPLICATION OF TRINITRONAPHTHALENE

Trinitronaphthalene is similar to dinitrobenzene as regards its explosive power.

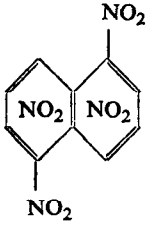
Before and during World War I it was fairly widely used, first in France and later in Germany, for filling shells, mostly in fusible mixtures with TNT.

Initially it was known as "Naphtite", later as "Trinal". Its other names are TN and TNN.

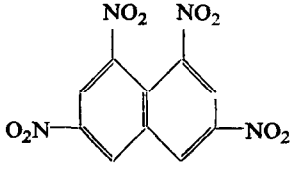
The maximum rate of detonation of trinitronaphthalene is about 5140 m/sec (Calvet [32]).

TETRANITRO DERIVATIVES OF NAPHTHALENE

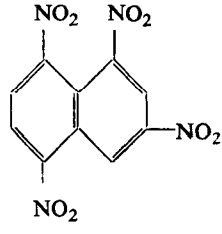
Five isomers of tetranitronaphthalene are known from the literature: the α– isomer, the position of two nitro groups in it being unknown, the β– (or 1,3,6,8-), the γ– (1,3,5,8- or 1,4,6,8-), the 6- (1,4,5,8-) and the 1,3,5,7-isomers:



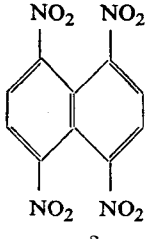
α
m. p. 259°C



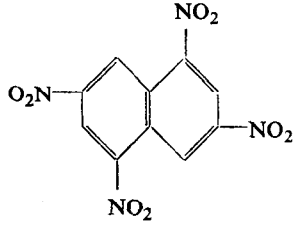
β
m. p. 203°C



γ
m. p, 194-195°C



δ
m. p. 340-345°C



m. p. 260°C
decomposition 263-265°C

The isomer δ was originally thought to be 1,2,5,8-tetranitronaphthalene (Will [17]). This was corrected by Dimroth and Ruck [18a]).

Each of them forms fine sand-coloured crystals, dissolving with difficulty in organic solvents. Some of them (e.g. 1,3,5,8-) are readily soluble in acetone. Concentrated sulphuric and nitric acids are the best solvents for them.

By the nitration of commercial dinitronaphthalene a product is obtained which consists of the 1,3,6,8-, 1,3,5,8- and 1,4,5,8-isomers. The existence of the α– isomer is not quite certain. It was reported by d'Aguiar [14], who obtained it by the prolonged boiling of 1,5-dinitronaphthalene with nitric acid (sp. gr. 1.45). The experiments were repeated by Beilstein and Kuhlberg [15] with a mixture of nitric and sulphuric acids instead of the nitric acid alone. However, Will's investigations [17]

did not confirm the results obtained by the above authors. Under the conditions they described Will obtained a mixture of the 1,3,5,8- and 1,4,5,8-isomers. He separated them by taking advantage of their different solubility in acetone. The 1,3,5,8-isomer is readily soluble even in cold acetone, while the other is insoluble even on boiling.

Lautemann and d'Aguiar [34], by boiling 1,8-dinitronaphthalene with nitric acid for 8 hr, obtained 1,3,6,8-tetranitronaphthalene. This result has been confirmed by Will.

As Patart reports, naphthalene can be nitrated to tetranitronaphthalene with mixtures containing only a small quantity of water:

HNO_3	30-45%
H_2SO_4	50-65%
H_2O	5%

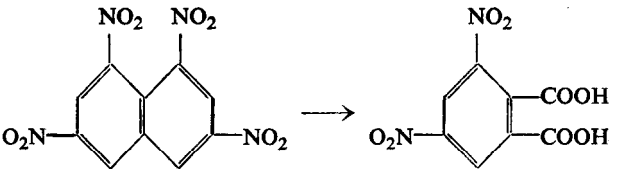
Starting from dinitronaphthalene more dilute nitrating mixtures may be applied :

HNO_3	10-95%
H_2SO_4	5-80%
H_2O	0-10%

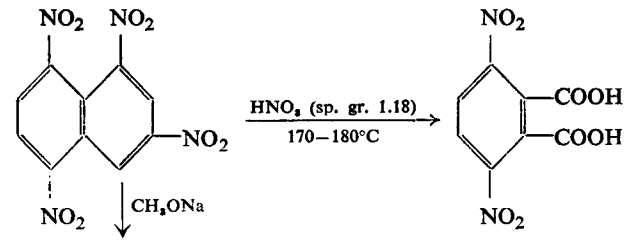
STRUCTURE OF TETRANITRONAPHTHALENES

Will has determined the structure of the 1,3,6,8- and 1,3,5,8-isomers by direct oxidation, or by oxidation of the products formed when reacting the isomers with sodium alcoholate.

Oxidation of 1,3,6,8-tetranitronaphthalene:



Oxidation of 1,3,5,8-tetranitronaphthalene:

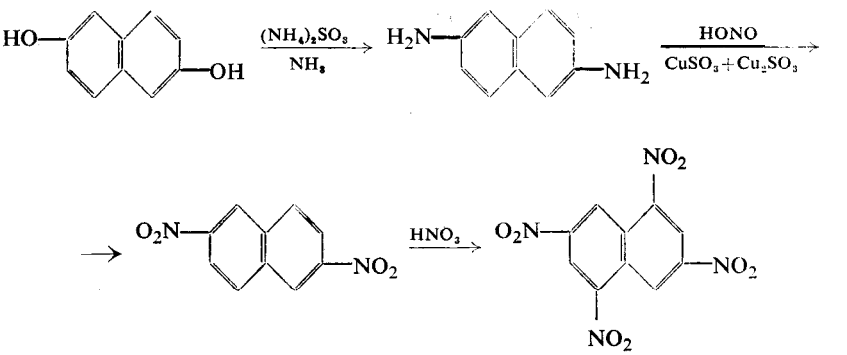


(6)

(7)

Due to difficulties in preparation, tetranitronaphthalenes are not applied as explosives.

1,3,5,7-Tetranitronaphthalene has been prepared (Chatt and Wynne [35]), by an indirect method:



(8)

THERMOCHEMICAL PROPERTIES OF NITRONAPHTHALENES

Rinkenbach [36] determined the heats of formation and heats of nitration from his measurements of heats of combustion of nitronaphthalenes. The heats of combustion of these compounds measured by Badoche [37] are in agreement with the values reported by Rinkenbach (Table 97).

TABLE 97

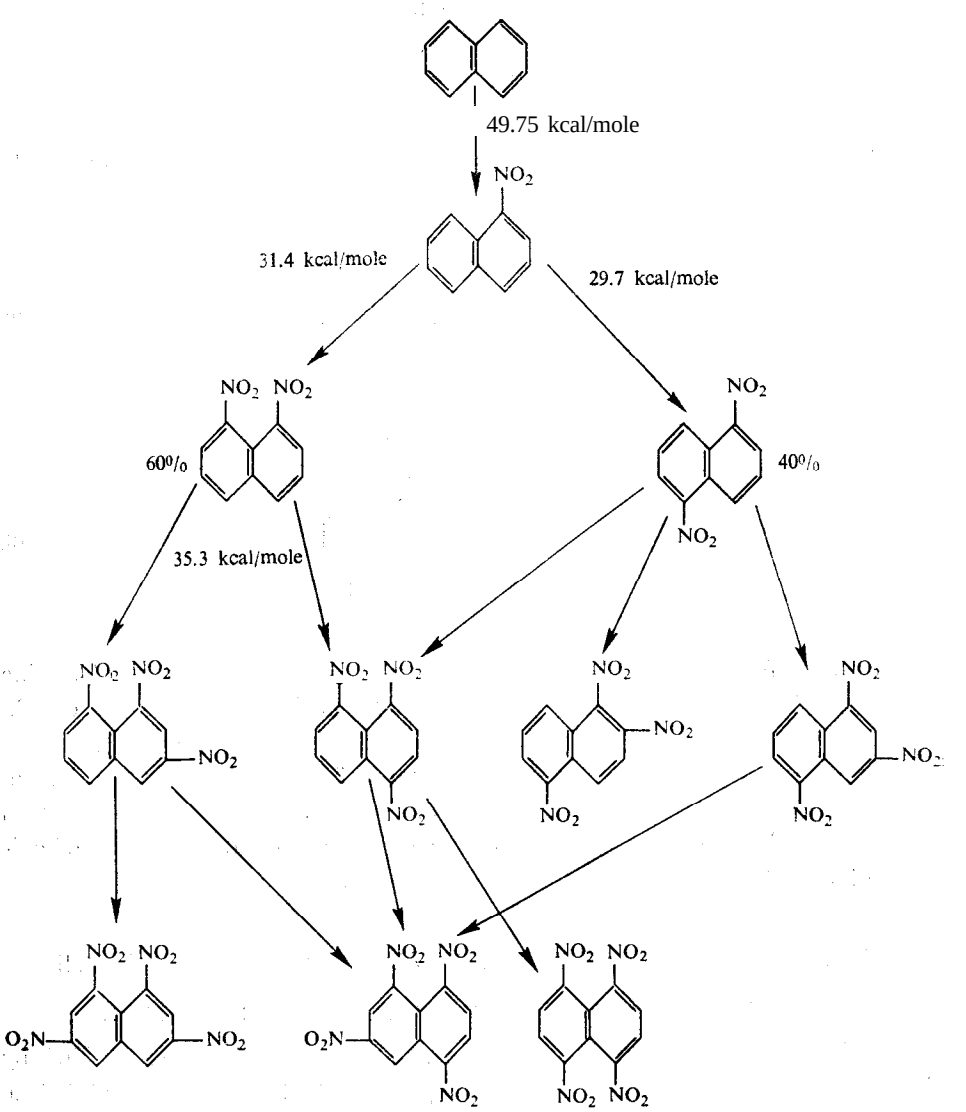
HEATS OF COMBUSTION AND FORMATION OF NITRONAPHTHALENES

Nitro derivative of naphthalene	Heat of combustion (after Badoche) at constant volume kcal/mole	Heat of formation (after Rinkenbach) kcal/mole
α– Nitronaphthalene	1190	-7.15
1,5-Dinitronaphthalene	1152	-5.44
1,8-Dinitronaphthalene	1154	-2.65
1,3,8-Trinitronaphthalene	1118	+5.7
1,4,5-Trinitronaphthalene	1121	-

Hence, the heats of nitration are:

naphthalene to α– nitronaphthalene	49.75 kcal/mole
α– nitronaphthalene to 1,5-dinitronaphthalene	29.67 kcal/mole
α– nitronaphthalene to 1,8-dinitronaphthalene	31.40 kcal/mole
1,8-dinitronaphthalene to 1,3,8-trinitronaphthalene	35.28 kcal/mole

A diagrammatic presentation of the nitration of naphthalene:



SIDE REACTIONS IN THE NITRATION OF NAPHTHALENE

Nitration of naphthalene, and higher stages of the nitration (e.g. trinitration) in particular, are accompanied by oxidation reactions which are manifested by the evolution of large quantities of nitrogen oxides.

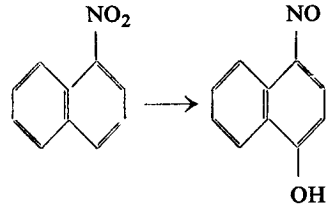
As a result nitrophthalic acids are formed, namely nitro- and dinitro-phthalic:

$C_6H_3.NO_2(COOH)_2$
$C_6H_2(NO_2)_2(COOH)_2$

Since under the conditions of the above reaction partial decarboxylation may take place, nitrobenzoic acids may also be formed:

$$C_6H_4.NO_2.COOH$$
$$C_6H_3(NO_2)_2COOH$$

In addition nitronaphthols are obtained, which may be formed either by direct oxidation or through isomerization of nitronaphthalenes to nitrosonaphthol or its derivatives :



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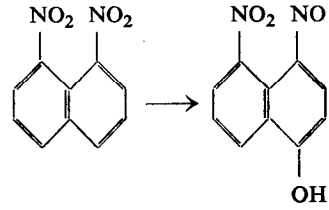


(10)

It has been found that such reactions can occur under the influence of fuming sulphuric acid, at 40-50°C. Nitrosonaphthol may then by oxidized to nitronaphthol. Moreover, picric acid may be formed during the nitration processes.

Resinous amorphous, brown substances are also formed, and found in dinitro- and trinitro-naphthalenes. They are partly soluble in alkalis, hence the suggestion that they are of an acidic or phenolic character and come from products of oxidation of naphthalene.

MANUFACTURE OF NITRO DERIVATIVES OF NAPHTHALENE

NITRATION OF NAPHTHALENE TO MONONITRONAPHTHALENE

Nitration grade naphthalene should be almost chemically pure, purified by sublimation or crystallization (pressed naphthalene). Sublimated naphthalene should not melt below 79.6°C, while the melting point of the pressed product (in lumps, 2-4 cm) should not be lower than 79.0°C.

With concentrated sulphuric acid the naphthalene should not produce a darker shade than a pale reddish pink.

German method

This method has been applied at I. G. Leverkusen. It consists in charging naphthalene into a nitrator, containing a part of the spent acid and nitronaphthalene from the previous batch. To this the nitrating acid is added.

The succession of operations is as follows. A cast iron nitrator of 7 m^3 capacity

is charged with 2500 1. of a mixture of spent acid and nitronaphthalene from the previous batch, warmed to 50-55°C. 1100 kg of naphthalene is added during about 15 min, while the nitrator contents are stirred. During this operation the temperature falls to 40-43°C. Then 800 1. of a nitrating mixture of the composition:

HNO_3	33%
H_2SO_4	47.5%
H_2O	19.5%

(sp. gr. 1.625-1.635 at 20°C) is added during 3 hr, the temperature rising by the end of the procedure up to 45°C. Then the rest of the naphthalene and acid are added during about 8 hr, in five lots: four of 200 kg each, alternating with 200 1. batches of the nitrating mixture, then the last of 300 kg of naphthalene, followed by 450 1. of the acid. In all, 2200 kg of naphthalene and 2050 1. (3300 kg) of the nitrating mixture is charged into the nitrator.

The temperature may rise during this period to 55°C. After all the acid has been added, the nitrator contents are stirred for another half an hour at 55°C and a sample is taken.

The nitronaphthalene precipitated by cooling, after washing with water should not melt below 51°C and should not smell of naphthalene. If the test is satisfactory, a part of the mixture in the nitrator is conveyed to a separator and the remaining 2500 1. is left for the next batch. The latter quantity is controlled by the depth of immersion of the pipe that conveys the mixture to the separator. The whole nitration process takes 12 hr.

Separation. Separation of nitronaphthalene from spent acid is effected in a cast iron separator, heated by a steam jacket, which permits the temperature to be maintained at 50-55°C. The separation of the mixture into two layers requires 3 hr. Then the lower layer of the spent acid is drawn off to an intermediate tank of 10 m^3 capacity and is allowed to cool. As a result, unreacted naphthalene collects at the surface as a crystalline mass. It is skimmed off mechanically.

Spent acid of the composition:

H_2SO_4	63%
HNO_3, NO_2	trace
H_2O	about 37%

is sent to be concentrated.

Granulation and washing. The molten nitronaphthalene in the separator is drained off to a granulator, previously charged with 6000 1. of cold water. During the introduction of nitronaphthalene compressed air is passed through the grantlator to agitate the water. This causes the nitronaphthalene to solidify in the form of granules. The granulation process requires one hour, then the flow of air is stopped and the water is drawn off through a siphon. The siphon pipe inlet is provided with a wire gauze to prevent the nitronaphthalene from being carried away. When the first portion of water has been drained off the nitronaphthalene left is agitated with new portions of water (6000 1. each) until neutrality (Congo red test). Usually 2-3 washings are sufficient. The washing process requires about 6 hr.

Then the vessel is charged with 1000-2000 1. of water and 100 kg of sodium carbonate and the whole is heated with live steam until the nitronaphthalene becomes molten. This requires about 2 hr. The water should remain alkaline towards phenolphthalein. The contents of the vessel are pumped to one of three washing tanks. The tank are made of sheet iron and equipped with a steam heater and with a stirrer (40 r. p. m). After 2 hr of agitation the lower layer (molten nitronaphthalene) is pumped into the next tank charged with a solution of 50 kg of sodium carbonate in 3000 1. of water and heated up to 85-95°C.

The molten nitronaphthalene is pumped to the last tank and is washed there with 3000 1. of water having a temperature of 85-95°C during 2-3 hr. The separation of the nitro compound from water requires 2 hr. The washed, molten nitronaphthalene is transferred to a drying kettle, where after being heated up to 95-105°C it is allowed to remain for 4 hr under reduced pressure (about 200 mm Hg), while constantly stirred (28 r. p. m).

Pure nitronaphthalene is sent, while still molten, for the preparation of α– naphthylamine by reduction.

If α– nitronaphthalene is to be used for preparing explosive compositions, it is poured off from the drying kettle into pans for solidification and then broken up into lumps.

From the quantities of raw materials given above, 2920 kg of nitronaphthalene (m. p. 52-52.5°C) are obtained. This corresponds to a yield of 132.5 kg of nitronaphthalene from 100 kg of naphthalene, i.e. 98% of the theoretical.

French method

The nitration of naphthalene to nitronaphthalene, according to Pascal [20a], is effected in a nitrator of the type shown in Fig. 108. The nitrator (1.16 m in diameter, 1.0 m high) is made of cast iron. The lower, conical part is provided with an outlet 5 cm in diameter, closed by a valve. The sheet iron jacket on the cylindrical part of the nitrator may serve a double purpose: cooling the nitrator contents by water or heating by steam.

The lid is provided with a rectangular opening (1) (35 x 20 cm) for feeding in the naphthalene. After the nitrator has been charged the opening is closed with a sheet iron lid. The nitrator lid is also equipped with pipe (2), connected with a ventilator by means of a stoneware pipe; the ventilator itself is connected with an absorption tower for absorption of nitrogen dioxide in water. In addition the nitrator is equipped with stirrer (3) (85-90 r. p. m) and with two baffles (4) located opposite to each other to increase the stirring effect.

In the nitrator described 300 kg of naphthalene can be nitrated in one batch.

The nitrator is charged with 1100 kg of a nitrating mixture of the composition :

HNO_3	12-14%
H_2SO_4	40-50%
H_2O	36-48%

The mixture is prepared from 600 kg of the spent acid from the dinitronaphthalene manufacture and 550 kg of the spent acid from mononitration, which has been re-used for washing dinitronaphthalene. In consequence the spent acid contains some of the HNO_3 adsorbed by dinitronaphthalene. The composition and the quantity of the mixture should be so calculated as to contain 128 kg of HNO_3, required for complete nitration of 300 kg of naphthalene.

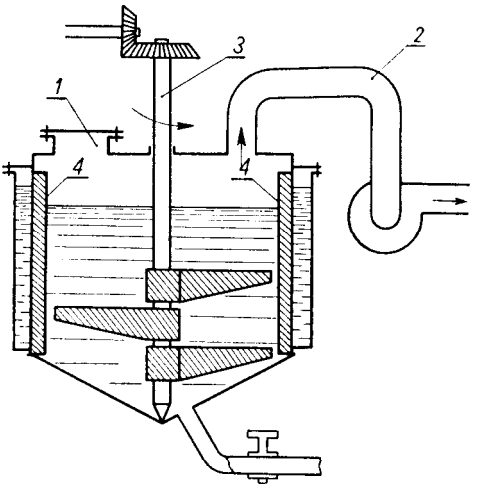


FIG. 108. Diagram of a nitrator for the nitration of naphthalene (Pascal [20a]).

The naphthalene to be nitrated (300 kg) is added to the nitrating mixture during aperiod of 3 hr. Meanwhile the temperature has risen spontaneously up to 50°C. When all the naphthalene has been added, the nitrator contents are heated to 55°C.

After the completion of the nitration process, the mixture in the nitrator is allowed to remain at rest to separate into two layers. Then the lower, acid layer is drawn off into a lead lined tank (I) (Fig. log), 1.5 m high and 1.25 m in diameter. Molten

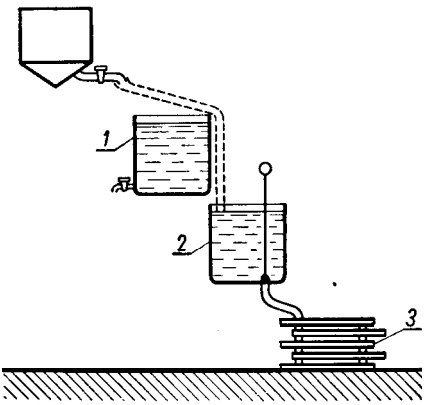


FIG. 109. Flow sheet of the nitration of naphthalene to nitronaphthalene (Pascal [20a]).

nitronaphthalene is drawn off through a lead or aluminium pipe into a similar tank (2), containing water heated by live steam to 70°C and is stirred for half an hour. The lower layer (molten nitronaphthalene) is then drained off into pans (3) arranged in the form of a stack, where it solidifies.

In this way 400 kg of the raw product ready for further nitration are obtained.

NITRATION OF NAPHTHALENE TO DINITRONAPHTHALENE

German method

The direct nitration of naphthalene to dinitronaphthalene by the method applied at I. G. Ludwigshafen is carried out in the following way:

A cast or wrought iron jacketed nitrator (of 3.4 m^3 capacity), equipped with a propeller stirrer (25-26 r. p. m), is charged with the following quantities of acids:

925 kg of 98% H_2SO_4
610 kg of 53% HNO_3
25 kg of 98% HNO_3

a nitrating mixture of the composition:

HNO_3	22.3%
H_2SO_4	58.1%
H_2O	19.6%

being obtained.

As heat is generated during stirring the temperature of the mixture rises to 30°C. Then 295 kg of naphthalene is introduced through a screw metering tank at a rate of 14.75-11.8 kg/hr. The naphthalene is added in the following way:

59	kg	during	the	first	4	hr	at	34-36°C
118	„	„	„	„	8	„	„	36-37°C
59	„	„	„	„	4	„	„	37-38°C
59	„	„	„	„	5	„	„	38-44°C

After adding all the naphthalene, the temperature is raised during a period of 4 hr up to 80°C and the nitrator contents are kept at this temperature for another hour.

The raising of ihe temperature is necessary for keeping the product of nitration in a molten state, as at this stage it consists of nitro- and dinitro-naphthalenes. The contents of two nitrators are pumped to a lead-lined stirred tank (of 14.9 m^3 capacity) containing 7000 1. of cold water. The temperature in the tank rises to 40-50°C. Due to constant stirring the product is kept in the form of droplets which, after cooling to 30°C, solidify giving sand-coloured granules. The contents of the tank are then conveyed to a vacuum filter of an area of 8 m^2 (6 m^3 capacity).

The spent acid, containing 30% of H_2SO_4 (sp. gr. 1.220) is disposed to a drain. The product on the filter is washed with 6 m^3 of cold, then with 12-14 m^3 of warm water.

French method

The nitration of naphthalene to dinitronaphthalene (after Pascal [20a]) is effected in a nitrator essentially of the same type as that used for the nitration of naphthalene to nitronaphthalene by the French method (Fig. 108, p. 441), the only difference being in the outlet which is wider at the bottom - 8 cm in diameter - since the nitration product is solid.

The nitrator is charged with 1060 kg of a nitrating mixture of the composition:

HNO_3	23-24%
H_2SO_4	54-55%
H_2O	21-21.5%

Then finely ground and sifted naphthalene is added at a rate which at the beginning is about 50 kg/hr, and by the end 35-40 kg/hr. During the addition of naphthalene the temperature is controlled by cooling, so that it does not exceed 55°. By the end of the process the mixture has heated up to 70°C.

After the completion of the reaction, the nitrator contents are discharged into a lead vacuum filter of 1000 1. capacity for separating the product from the spent acid. The spent acid has the composition:

HNO_3	0.5-1.5%
NO_2	1.5-2.5%
H_2SO_4	62-63%
H_2O	33-35%
organic matter	ca. 1.5%

The product is washed as described below (see preparation of dinitronaphthalene from nitronaphthalene).

NITRATION OF NITRONAPHTHALENE TO DINITRONAPHTHALENE

French method

As Pascal [20a] reports, the reaction is carried on in the following way. The nitrator is fed with 1150 kg of a nitrating mixture of the composition:

HNO_3	26.5%
H_2SO_4	51%
H_2O	22.5%

Then during 3-4 hr 400 kg of α– nitronaphthalene is added in lumps obtained by breaking with a hammer the product of mononitration. The temperature is maintained within the range 38-45°C by cooling. A ternary eutectic formed by α– nitronaphthalene and 1,5- and 1,8-dinitronaphthalenes melts within the range 44-54°C, So that at this stage of the process the substance being nitrated is in a molten state, thus facilitating nitration. A stirrer keeps the substance in suspension in the form of drops of l-2 mm in diameter.

After all the nitronaphthalene has been added, the temperature is raised to 55°C within one hour, and then cooled to 40°C. The dinitronaphthalene solidifies in the form of granules.

The nitrator contents are drawn off to the filter tank (1) (Fig. 110). The tank is lead-lined and equipped with a ventilating pipe for conducting away nitrogen oxide. Filtration is most effective with a 20-cm layer of coarse-grained dinitronaphthalene as a filter material, placed between perforated plates of sheet aluminium.

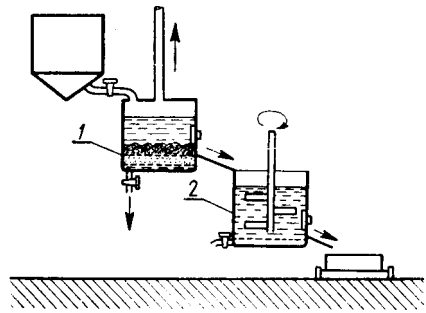


FIG. 110. Flow sheet of the nitration of nitronaphthalene to dinitronaphthalene (Pascal [20a]).

Nearly 60% of the spent acid (600 kg) of composition:

HNO_3	14.5%
H_2SO_4	56.5%
H_2O	29%

flows off from the dinitronaphthalene and is recycled to the nitration of naphthalene to nitronaphthalene. The rest remains in the dinitronaphthalene and can be recovered by washing the latter with the spent acid from mononitration (containing only insignificant quantities of nitric acid and nitrogen oxides). The recovered acid is mixed with the nitrating mixture for the nitration of naphthalene to nitronaphthalene.

The acid-washed dinitronaphthalene is washed six times with water, each time the filter tank being filled with cold water up to the brim. Then dinitronaphthalene is discharged through a side opening into double bottomed wooden vat (2), containing water heated to 60°C. After six washings with hot water, the product is discharged through a side opening and loaded into trucks.

The water content in washed dinitronaphthalene is 25%; the product is dried in dryers, which may be of various construction, until the content of water falls to 0.5%.

The two-stage nitration of naphthalene to dinitronaphthalene requires more complex plant and is more labour consuming: nevertheless it is more economic than single stage nitration, since the product obtained is of higher purity, more easily freed from acid, and the consumption of nitric acid is lower.

The following data given by Pascal illustrate the superiority of two-stage nitration (Table 98).

TABLE 98

MATERIAL CONSUMPTION FOR 1000 kg OF DINITRONAPHTHALENE

Material	One-stage nitration, kg	Two-stage nitration, kg	Calculated theoretical quantity, kg
Naphthalene	625	612	587
HNO_3 (100%)	739	637	579
H_2SO_4 (100%)	732	684	-

The possibility of recovering nitric acid from vapours carried away through the ventilator has not been taken into account.

According to Gorst [31] three grades of DNN are specified in the U.S.S.R. (OST 2940) (Table 99).

TABLE 99

	Grade I	Grade II	Grade III
General appearance	DNN should be a uniform powdery or granular material free from foreign inclusions		
Setting point, °C	150	150	150
Moisture and volatile matters, max.	0.5%	0.5%	0.5%
insoluble in acetone-xylene mixture, max.	0.2%	0.3%	0.5%
Ash total, max.	0.2%	0.2%	0.3%
containing: SiO_2 max.	0.05%	0.05%	0.05%
Pb	-	traces	0.03%
Fe	traces	traces	
Acidity (% H_2SO_4)	0.1%	0.1%	0.2%

NITRATION OF NITRONAPHTHALENE TO TRINITRONAPHTHALENE

French method [31a]

At the St. Chamas plant, the nitrator is of 4 m^3 capacity, equipped with a propeller stirrer (100 r. p. m.) and with a jacket for cooling or heating. There is an outlet 80 mm in diameter at the bottom of the nitrator for discharging the contents.

The nitrator is charged with 800 kg of the spent acid from trinitration and 1330 kg of a mixture:

HNO_3	40%
H_2SO_4	55%
H_2O	5%

This mixture has an exceptionally high content of nitric acid, which is of great importance to obtain the required high degree of nitration.

900 kg of molten nitronaphthalene direct from the nitrator, together with 2600 kg of the above nitrating mixture, is run into the nitrator. The introduction of nitronaphthalene and acid requires about 8 hr. During this procedure a temperature of 57°C is maintained. Then the nitrator contents are stirred for 2 hr at 57°C. After cooling to 40°C during a period of 4 hr the nitrator is discharged at the bottom. During the cooling process the product solidifies to form granules, which can easily be atered off from the acid on a vacuum filter.

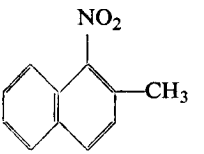
It may happen that trinitronaphthalene becomes lumpy during cooling, thus rendering discharge difficult. If this occurs, the nitrator contents should be reheated to 57°C and then slowly cooled to 45°C prior to being discharged. If this proves ineffective a considerable part of the acid is removed from the nitrator (the acid being the lower layer and trinitronaphthalene the upper), and in its place spent acid from mononitration is introduced. The mixture is then heated to 50-60°C and even to 70°C (the temperature should be the higher the more the mononitration acid has been used) and drawn off into a filter. The filtered nitration product is transferred to a tank containing water. During washing the lumpy material disintegrates, forming granules.

The end product usually contains about 15.6% of nitrogen (the lowest content admissible is 15.1%), while the theoretical content should be 15.97% of N. The melting point of the product ranges from 108°C at the beginning to 124°C by the end of melting.

Although the process is carried out at low temperature it is not quite safe. At the St. Chamas factory an explosion of the nitrator contents occurred in 1940. The accident was caused by a fault in the stirrer. Shortly before the explosion took place an evolution of brown nitrogen oxides had been observed, as well as a local temperature rise up to 77°C, which meant it was 20°C too high. Inflammation of the product in the nitrator then followed.

After the accident additional agitating equipment for mixing with compressed air was installed, as a stand-by for use in the event of a breakdown of the stirrer.

2-METHYL-1-NITRONAPHTHALENE



m. p. 81°C

Since 2-methylnaphthalene has been made available through improvements in coal tar separation methods, considerable interest in the derivatives of this hydrocarbon has been recently shown. Nitration is obviously one of the ways of transforming this raw-material into products of greater commercial application.

As long ago as 1884, Schulze [38] examined the process of nitration of 2-methylnaphthalene with nitric and sulphuric acids and reported 1-nitro-2-methylnaph-

thalene, a dinitro-product and an oil as the products of nitration. Medinaveitia and de Buruaga [39] also used a mixture of nitric and sulphuric acids and obtained polynitro compounds.

A number of other authors have carried out the nitration of 2-methylnaphthalene, mainly as a step in the preparation of a new intermediate for dyes. Lesser, Glasser and Aczel [40] nitrated 2-methylnaphthalene in the presence of acetic acid and Vessely and Kapp [41] used nitric acid alone at low temperature (5-15°C). They obtained a 58% yield of 1-nitro-2-methylnaphthalene and an oil which contained 4-Nitro-, 6-nitro- and 8-nitro-2-methylnaphthalenes. Vessely and his co-workers [42, 43] identified qualitatively most of the mononitro derivatives of 2-methylnaphthalene and their reduction products.

The most extensive work on the subject so far has been carried out by Brink and Shrieve [44]. The highest yield of 2-methyl-1-nitronaphthalene they obtained was 57% of the theoretical. This was produced by nitrating 2-methylnaphthalene at low temperatures (0-30°C) with a 70% excess of 70% nitric acid. The other isomers appeared as a by-product oil. When using a 15% excess of a nitrating mixture composed of 25% HNO_3, 55% H_2SO_4 and 20% H_2O the yield of l-nitro-2-methylnaphthalene was also 57%. Dinitration took place when acetic anhydride was used. The product was in the form of a solid with m. p. 209-213°C. No determination of the structure of the dinitroproducts was carried out.

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CHAPTER XII

NITRO DERIVATIVES OF HALOGENOBENZENES

APART from a few exceptions nitro derivatives of halogenobenzenes are not used as explosives. Nevertheless they are, or may be, important intermediates in the manufacture of explosives, dyes and drugs.

Derivatives of chlorobenzene are of course the most important, as they are the most readily available. For certain syntheses nitro derivatives of fluoro- or bromobenzene are used. They may be of value sometimes, since the former are less reactive and the latter more reactive than chlorobenzene derivatives. For example, recently 2,4-dinitrofluorobenzene has been widely applied in the elucidation of the structure of peptides (Sanger [1]).

Ingold and Bird [2] investigated the rates of nitration of fluoro-, chloro-, bromo- and iodo-benzenes with acetyl nitrate and found that they could be arranged in the following order: 1: 0.15: 0.033: 0.030: ca. 0.18 (taking the relative rate of nitration of fluorobenzene as unity).

The kind of halogen atom affects the substitution in the ring with the nitro group. Table 100 shows the results of investigations by Sandin and J. R. W. Williams [3]. J. D. Roberts and co-workers [3a] obtained similar results by using isotope dilution analysis.

TABLE **100**

Compound	Halogenonitro compound		
	ortho	*para*	*ortho/para* ratio
C_6H_5F	12.6	87.4	0.14
C_6H_5Cl	30.1	73.1	0.41
C_6H_5Br	37.2	62.5	0.59
C_6H_5I	34.2	65.8	0.52

This trend has been explained in a satisfactory manner by the rule established by Lapworth and Robinson [4]: the increase in relative yield of the ortho-product parallels the decrease in the negative inductive influence of the halogens. The induc-

tive effect which opposes substitution is felt most strongly at the ***ortho*** position.

Ingold [5] summarized his experiments on the rate of substitution. Some rates of nitration which were calculated relative to the total rate for benzene, taken as unity, are given in Table 101.

TABLE 101

Benzene	1	Fluorobenzene	0.15
Toluene	24.5	Chlorobenzene	0.033
Ethyl benzoate	0.00367	Bromobenzene	0.030
Benzyl chloride	0.302	Iodobenzene	0.18

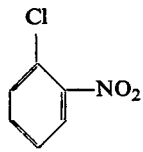
NITRO DERIVATIVES OF CHLOROBENZENE

Chloronitro compounds are nearly always obtained by nitration of the corresponding chlorinated hydrocarbons. Picryl chloride, for example, a trinitro derivative of chlorobenzene, may be prepared by direct nitration. This possibility has in the past aroused some interest in picryl chloride as an explosive. It was indeed manufactured and used in small quantities in Germany during World War I but in the long run did not achieve any importance as a high explosive, mainly because of its high reactivity and its readiness to yield picric acid and, with metals, picrates. Picryl chloride may be a useful starting material in the preparation of several higher nitrated derivatives of diphenyloxide (p. 549) and diphenylamine. Nitro derivatives of *p*- dichlorobenzene (p. 466) were also used during World War I as high explosives.

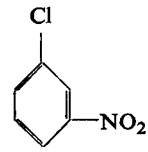
The nitration of chlorobenzene was first mentioned in 1862 by Riche [6]. Later the reaction was studied by Sokolov [7] and Holleman and de Bruyn [8]. Junglleisch [9] was the first to describe the method of preparation of chlorodinitrobenzene from *o*- or *p*- chloronitrobenzene. Laubenheimer [10] investigated the products of the nitration of *m*- chloronitrobenzene, and Ostromyslenskii [11] determined the structure of the products obtained by Jungfleisch, i.e. of 1,2,4- and 1,2,6-chlorodinitrobenzenes. Finally in 1894 the Griesheim factory reported [12] on a method of preparing chlorotrinitrobenzene by direct nitration of chlorobenzene.

MONONITRO DERIVATIVES OF CHLOROBENZENE

There are three chloronitrobenzene isomers known: *ortho, meta and para:*



m. p. 32.5°C
b. p. 245°C



m. p. 46°C
b. p. 235°C

m. p. 83°C
b. p. 242°C

The *o*- and *p*- isomers can be obtained during the nitration of chlorobenzene. The higher the nitration temperature, the more *o*- isomer is formed.

As Holleman and de Bruyn [8] reported:

At 0°C 30.1% of the *ortho*- and 69.9% of the *para*- isomer is formed, at 30°C 26.9% of the *ortho*-, and 73.1% of the para-isomer is formed. Besides, higher temperatures favour the formation of some small quantities of *m*- chloronitrobenzene. The product is prepared commercially mainly by chlorination of nitrobenzene in the presence of ferric chloride.

According to other authors (McCormack [13]; Dey and co-workers [14]), the *para*- to *ortho*- isomer ratio varies from 66/34 to 64/36, depending on the nitration-conditions.

Bieber and Schuring [15] carried out extensive investigations into the mono-nitration of chlorobenzene. Mixtures of nitric and sulphuric acids were used and variables included the nitric acid content in the nitrating acid, the ratio of nitric acid to chlorobenzene, the sulphuric acid concentration and the nitration temperature.

In the range of conditions investigated, concentration of nitric acid and the ratio of nitric acid to chlorobenzene had little influence on the final distribution of the chloronitrobenzene isomers. The ratio between *p*- and *o*- isomers varied between 63/37 to 70/30. The temperature effect can be seen from the figures for runs with a final concentration of H_2SO_4 of 80% and 70%:

	80%	70%
at -5°C the ratio was	70.5 / 29.5	-
at 50°C „ „	65.6 / 34.4	61.1. / 32.3
at 90°C „ „ „	63.4 / 36.6	65.6 / 34.4

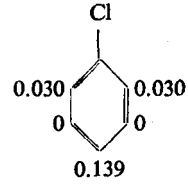
The formation of *p*- chloronitrobenzene could be related to the sulphuric acid concentration and nitration temperature (t) by the equation:

$$\%\ p\text{- ChloroNB} = [0.13 - 0.0027\ S]\ t + 70.6 \qquad (1)$$

where S is % of H_2SO_4.

The content of *m*- chloronitrobenzene varied from 0 to 1.5% apparently increasing with temperature.

According to Ingold and Bird [2] the rate of nitration of each nuclear position can be illustrated by the diagram:



in which unity represents rate of attack on one nuclear position of benzene.

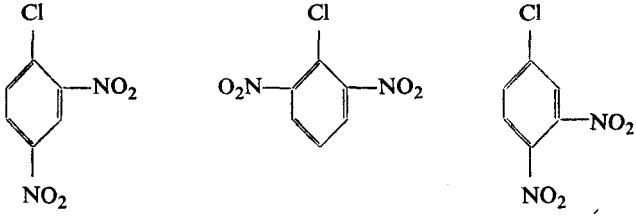
For preparing 1,2,4-chlorodinitrobenzene of high purity, *p*- chloronitrobenzene should be used as starting material since mixtures of *o*- and *p*- chloronitrobenzenes yield mixtures of two dinitro-isomers, namely, 1,2,6- and 1,2,4,-. The corresponding reactions are shown in the diagram on p. 465.

The chloronitrobenzene isomers are highly toxic. Due to their high vapour pressures in summer time or in warm places the atmosphere may contain sufficient chloronitrobenzene to cause poisoning, which may sometimes be fatal. The maximum allowable concentration of chloronitrobenzene in the air is 0.001 mg/l., according to Lazarev [16].

Acute poisoning is characterized by symptoms similar to those appearing in poisoning by nitrobenzene. Lazarev [16] thought nerve paralysis might occur, as well as loss of reflex and tonic spasm. Skin irritation also takes place.

DINITRO DERIVATIVES OF CHLOROBENZENE

Among the six chlorodinitrobenzenes known, the 1,2,4- and 1,2,6-isomers are the most important as they are the principal products of the nitration of chlorobenzene. 1-Chloro-2,4-dinitrobenzene results from the nitration of *o*- and *p*- chloronitrobenzenes and 1-chloro-2,6-dinitrobenzene from the *o*- isomer. Apart from these, the 1,3,4-isomer, which forms in the nitration of *m*- chloronitrobenzene, is of some importance.



All these compounds are known to appear in more than one crystalline forms differing in their melting points. The 1,2,6-isomer can exist in the α– and β– forms (m. p. 92°C and 40°C respectively), and the 1,3,4-isomer in the α–, β–, and γ– forms (m. p. 36.3°C, 37.1°C, 28°C).

1-Chloro-2,4-dinitrobenzene

Physical properties. Three crystalline forms of 1-chloro 2,4-dinitrobenzene are known. A stable α– modification (m. p. 53.4°C) crystallizes from nitric acid (62%) or from alcohol. An unstable, β– modification (m. p. 43°C) can be precipitated, as Ostromyslenskii [11] reports, from a fuming nitric acid solution by treating it with water. It may also be obtained by rapid cooling of the molten substance.

Another unstable modification, γ, melting at 27°C, has also been isolated (Müller [17]).

The solubilities of 1-chloro-2,4-dinitrobenzene in various solvents are given (after Dévergnes [18]) in Table 102.

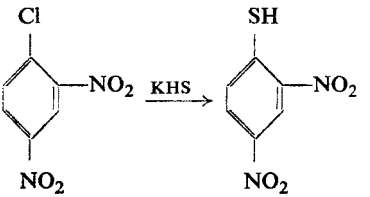
TABLE 102
SOLUBILITY OF 1-CHLORO-2,4-DINITROBENZENE

Solvent	g/100 g of the solvent			
	15°C			100°C
Water	0.0008	at 50°C	0.041	0.159
Methyl alcohol	11.226	at 32°C	32.31	
Ethyl alcohol abs.	8.246	at 32.5°C	18.89	
Ethyl ether	23.517	at 30.5°C	128.13	
Acetone	261.9	at 30°C	581.0	
Ethyl acetate	119.4	at 50°C	287.5	
Chloroform	102.76	at 32°C	210.0	
Carbon tetrachloride	3.851	at 31°C	28.87	
Carbon disulphide	4.212			
Benzene	158.43	at 31°C	359.64	
Toluene	139.89	at 31.5°C	282.55	
Pyridine	2.633	at 20°C	20.85	

In sulphuric acid of concentrations below 80%, 1-chloro-2,4-dinitrobenzene dissolves only with difficulty.

Chemical properties. A chlorine atom *ortho* or *para* to a nitro group is especially reactive and is readily substituted. Numerous examples of such reactions, utilized in the preparation of explosives, are given later in the descriptions of preparation methods for dinitrophenol, dinitroanisole, hexanitrodiphenylamine, hexanitrodiphenyl sulphone, dinitroaniline, tetryl, etc. Chlorodinitrobenzene reacts with sodium sulphide and sulphur to yield sulphur dyes. The action of sodium disulphide results in the formation of tetranitrodiphenyl sulphide (p. 554).

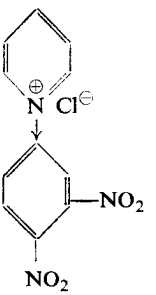
When treated with KHS in alcoholic solution chlorodinitrobenzene yields dinitrothiophenol :



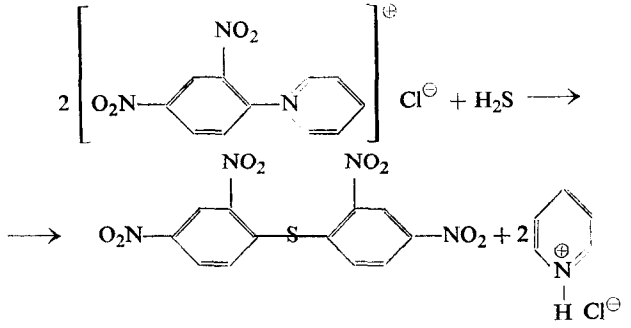
(2)

the reaction being of the nucleophilic substitution type.

Chlorodinitrobenzene reacts with pyridine to form dinitrophenylpyridinium chloride (Vongerichten [19]):

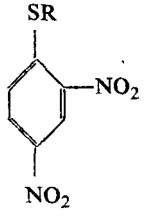


This highly reactive compound may be utilized for various reactions (Zincke [20, 21]). For example, with hydrogen sulphide it forms a tetranitro derivative of diphenyl sulphide (Zincke and Weisspfennig [22]).

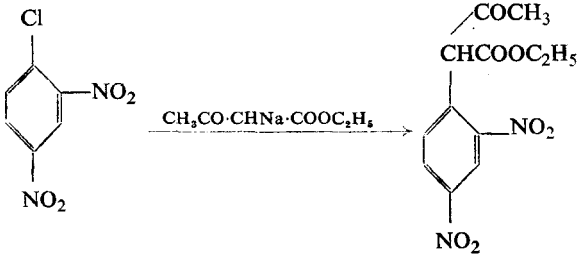


(3)

When reacted with mercaptans or thiophenols of the general formula RSH yields thioethers (Bielig and Reidies [23]):



Commercial 1-chloro-2,4-dinitrobenzene prepared by the nitration of a mixture of *o*- and *p*- chloronitrobenzenes usually contains the 1,2,6-isomer. The latter differs from the 1,2,4-isomer in some of its properties. According to Borsche and Rantscheff [24], only the 1,2,4-isomer can react with the sodium salt of acetylacetic ester, the 1,2,6-isomer remaining unchanged.



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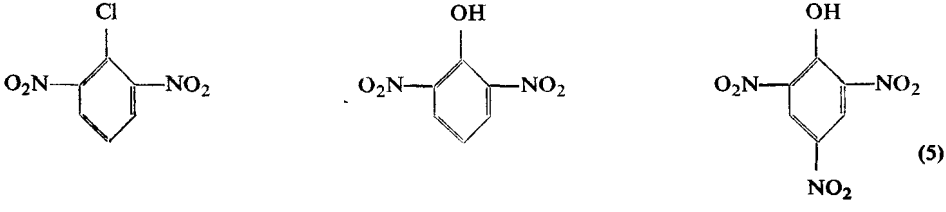
The structure of the 1,2,6-isomer has been determined by Ostromyslenskii [11] from the following reactions leading to picric acid:



(5)

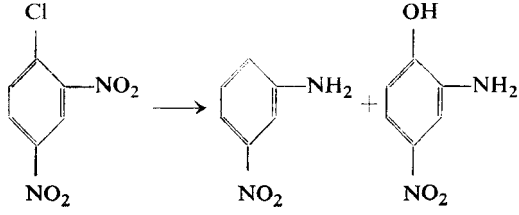
When using chlorodinitrobenzene in the manufacture of explosives, the products obtained from it (e.g. dinitroanisole, dinitrodiphenylamine) are nearly always subjected to further nitration. Both the 1,2,6- and 1,2,4-isomers then yield the same trinitro derivative, 1-chloro-2,4,6-trinitrobenzene. In such cases separation of the isomers and the preparation of highly pure 1,2,4-isomer is not necessary.

There are cases, however, where the presence of the two isomers makes process control difficult, i.e. when the process is controlled by determining the melting point of the product. Then *o*- and *p*- chlorodinitrobenzenes are separated, and only the latter is nitrated, pure l- chloro-2,4-dinitrobenzene being obtained.

Toxicity. The chlorodinitrobenzene isomers are highly toxic. Contact with the skin is especially harmful and provokes eczema. Smiriagin and Shapiro report (see Lazarev [16]) that out of 54 women working with their hands dipped in a liquid containing as little as 0.003% of 1-chloro-2,4-dinitrobenzene, all but 2 suffered from acute eczema after a month of exposure, and were unable to work for 8-23 days or even longer. Grave injuries may also be caused by inhaling the vapours of the hot substance or its dust. The maximum allowable concentration of chlorodinitrobenzene in the air is 0.001 mg/l, according to Lazarev.

Apart from skin injuries the symptoms of poisoning by chlorodinitrobenzene are similar to those produced by dinitrobenzene, namely general bodily weakness, cyanosis, a decrease of the number of red blood cells, disturbances in the functioning of digestive organs and heart failure. Treatment and recovery sometimes prove most difficult especially with regard to the digestive tract and the heart, whereas skin lesions are relatively easier to heal.

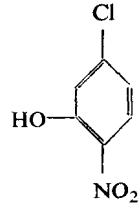
1-Chloro-2,4-dinitrobenzene is converted in the living body into *m*- nitroaniline and nitroaminophenol :



(6)

Both compounds can be determined colorimetrically, by diazotization followed by conjugation with β– naphthol.

The nitration reaction of chlorobenzene is usually accompanied by oxidation reactions, resulting in the formation of phenols, as for example, l-chloro-4-nitro-5-hydroxybenzene (2-nitro-5-chlorophenol) :



in the proportion of about 0.1%.

Other impurities which may be present in chlorodinitrobenzene are: chloronitrobenezenes, as products of an incomplete nitration, *m*- dinitrobenzene formed from benzene present in the chlorobenzene and chloropicrin.

MANUFACTURE OF *o*- AND *p*- CHLORONITROBENZENES

I. G. Griesheim method

At the Griesheim Works the following process was applied for nitrating chlorobenzene to *o*- and *p*- chlorodinitrobenzenes. A cast iron nitrator is charged with 6530 kg of a nitrating mixture of the composition:

HNO_3	30%:
H_2SO_4	56%
H_2O	14%

Then 3500 kg of chlorobenzene from the extraction stage of the process (as described below) is gradually run into the nitrator, with continuous stirring. The chlorobenzene should be of high purity, boiling at 132°C and distilling within a range of 0.5°. Initially a temperature of 40°C should be maintained and allowed to rise to 55°C by the end of the operation. The nitrator contents are then heated to 70-80°C during a period of 2 hr prior to transfer to a separator lined with acid resistant ceramic tiles. After the mixture has settled, the lower acid layer is drawn off to a special tank where it is stirred together with the chlorobenzene to be used for the next nitration. In this way part of the chloronitrobenzene dissolved in the acid, along with the remainder of nitric acid and nitrogen oxides, is extracted by the chlorobenzene.

The oily upper layer of chloronitrobenzene is washed with water, then with a sodium carbonate solution, and again with water, followed by drying under reduced pressure. Drying of the product is necessary to prevent corrosion of the crystallizers. In this way, 4850 kg of crude chloronitrobenzene (m, p. 52°C) are obtained, a yield equivalent to 98% of the theoretical.

I. G. Leverkusen method

4500 kg of chlorobenzene is charged into 2500 kg of waste acid from the previous batch in a nitrator of 10 m^3 capacity. Then 7100 kg of mixed acid containing:

HNO_3	35%
H_2SO_4	52.5%
H_2O	12.5%

is added with stirring and cooling, so that the temperature gradually rises in 9 hr from 20°C to 50°C. The contents are then stirred for 3 hr at 80°C.

A sample is taken to test the washed and dried product (m. p. min. 53°C). The spent acid should possess a density of 1.620 at 15°C; a content of HNO_3 less than 0.4% and of HNO_2 less than 0.4%. Usually the figures are 0.0% and 0.2% respectively.

If the test is satisfactory, the contents of the nitrator are left for 3 hr to settle, then the spent acid is drawn off through a sight glass into an extraction vessel of 10 m^3 capacity. The spent acid after cooling and settling, is transferred to a spent acid vessel of 18 m^3 capacity and from here, after standing, it is finally sent to the acid concentration plant.

The chlorobenzene from the extraction stage is used for the next nitration batch. Chloronitrobenzene is sent to a tile-lined, 10 m^3 washing tank. Here it is agitated three times with 3000 1. of water at 60-70°C by an air stream until neutral to Congo red. Then it is washed with 20 kg of sodium carbonate in 3000 1. of water, and finally with hot water to neutrality. The product is dried at 90-100°C under reduced pressure in a 7 m^3 drying vessel heated by a heating coil. The yield is 98% of the theoretical.

The product has a m. p. of 53-54°C with a dinitro compounds content below 0.1% and is free from nitrophenols. The spent acid contains 70% of H_2SO_4.

Separation of isomers. To separate *o*- and *p*- chloronitrobenzenes the Leverkusen Works crystallize large quantities (14,000-15,000 1. batches) of crude chloronitrobenzene in crystallizers of 15 m^3 capacity, equipped with two cooling coils (cooling area of 600 m2). The two coils are separated from each other by a horizontal, perforated plate. The crystallizer is charged with hot (80-100°C) crude chloronitrobenzene. The product is cooled down to 20°C during 25 hr, then the liquid eutectic mixture (6000-7000 1.) is drawn off through the tap at the bottom of the crystallizer, which takes about 8 hr. The crystalline residue in the crystallizer is washed three times with methyl alcohol (2000-4000 1. each time). The alcohol used for the first washing has already served twice for the same purpose. The second washing is done with alcohol which was used only once, while for the third one freshly distilled methyl alcohol is used. After being used three times the methyl alcohol is sent to a distillation unit, where it is re-distilled and then returned to the washing operation. The residue left after the alcohol is distilled off is added to the liquid eutectic.

The washed product left in the crystallizer is pure commercial *p*- chloronitrobenzene and should have a freezing point of 82-82.5% If not, an additional wash should be given.

The liquid eutectic goes to a distillation column where it is separated into fractions at a pressure in the receiver of about 10 mm Hg and at 180°C at the bottom of the column; the temperature in the dephlegmator is 100-120°C. The first fraction. I, is a mixture of chlorobenzene and chloronitrobenzene isomers (mainly *m*- chloronitrobenzene). The second, II, is rich in *p*- chloronitrobenzene. Finally the main fraction is distilled off, melting initially at 35°C and towards the end of distillation at 28°C. The last, III, is *o*- chloronitrobenzene of 90% purity.

From fraction I a mixture containing 72% of *m*- chloronitrobenzene and 28% of *p*- chloronitrobenzene is drawn off by distillation.

By treating this mixture with sodium hydroxide solution the *p*- isomer is converted to *p*- nitrophenol, while the ***m***- isomer remains unchanged.

Fraction II is recrystallized. From fraction III *o*- chloronitrobenzene is isolated by crystallization, effected by slow cooling to 15-18°C for about 80 hr.

The resultant crystals are not washed with methyl alcohol. The product melts at about 32°C. The crystallization liquor is added to that from the first crystallization.

At the Griesheim Works the isomers are separated in a similar way but using chlorobenzene for washing instead of methyl alcohol.

NITRATION OF *p*- CHLORONITROBENZENE TO l-CHLORO-2,4-DINITROBENZENE

According to the Griesheim method of nitration of *p*- chloronitrobenzene to l-chloro-2,4-dinitrobenzene, 4500 kg of molten *p*- chloronitrobenzene (m. p. 82.4°C) is introduced into a nitrator, followed by 5700 kg of a nitrating mixture,

HNO_3	35%
H_2SO_4	65%

with simultaneous stirring and cooling.

The cast iron nitrator of 8 m^3 capacity is equipped with a jacket and a lead coil.

Nitration starts at 95°C the temperature then being lowered to 45-55°C. After all the acid has been added the mixture is stirred for 2 hr at 65°C. Nitration is considered to be complete when a sample of the dry product solidifies at 49.6°C.

The mixture in the nitrator is then cooled to 55-60°C diluted. with 1000 kg of water, stirred and allowed to settle. Then the lower spent acid layer is drained off and mixed with chlorobenzene to recover nitrogen oxides and nitro compounds present in the acid. The chlorobenzene is then nitrated to chloronitrobenzene (as described above), while the spent acid goes to the concentration plant to obtain concentrated sulphuric acid.

The nitro compound layer is washed with warm water, then with a warm dilute solution of sodium carbonate and again with warm water. The washed nitro compound is dried by heating under reduced pressure. From 100 kg of *p*- chloronitrobenzene 128.5 kg of 1-chloro-2,4-dinitrobenzene is obtained, which is 98.5% of the theoretical yields.

NITRATION OF CHLOROBENZENE TO CHLORODINITROBENZENE (GRIESHEIM METHOD)

The nitration of chlorobenzene to chlorodinitrobenzene without separating the isomers of chloronitrobenzene is accomplished in two successive stages in the same nitrator.

Mononitration. 3000 kg of chlorobenzene, boiling within a range of 0.8°C, is mixed with the spent acid from dinitration, containing 78% of H_2SO_4. Then 1850 kg of a nitrating mixture of the compositions :

HNO_3	87-88%
H_2SO_4	11%

is added to the solution at 40-55°C, while stirring and cooling. The whole is heated to 70°C and stirred at this temperature for 2 hr. When nitration has been completed the stirrer is stopped and the mixture is allowed to remain at rest. After it has separated into two layers, the lower one - spent acid containing 70% of H_2SO_4 - is transferred to a tank of 13 m^3 capacity lined with acid resistant bricks, where it is agitated with chlorobenzene. The chlorobenzene, now containing chloronitrobenzne extracted from the spent acid, is used for nitration, while the acid freed from the nitro compound is concentrated.

Dinitration. 5100 kg of a nitrating mixture of the composition:

HNO_3	35%
H_2SO_4	65%

is run into the nitrator containing the chloronitrobenzene, a temperature of 50-55°C being maintained by cooling.

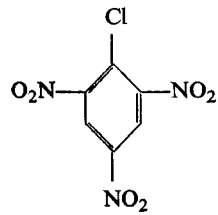
The whole is heated to 70°C and stirred for 2 hr at 70-80°C. Nitration is complete if a sample of the product has a melting point of 47.6°C, and, when steam distilled after being brought to alkalinity, the distillate does not smell of *o*- nitrophenol. After nitration has been completed, the whole is cooled to 50°C diluted at this temperature with 390 kg of water and allowed to remain at rest for separation. The lower spent acid layer, containing 78% of H_2SO_4 is used for mononitration.

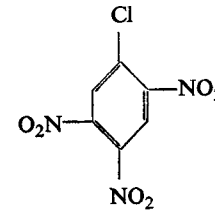
Chlorodinitrobenzene forming the upper layer is washed with warm water. then with a warm dilute solution of sodium carbonate and again with warm water, until entirely free from acid. Then it is dried by heating under reduced pressure in a 20 m^3 tank.

From 100 parts of chlorobenzene 175 parts of chlorodinitrobenzene with a melting point of 47.6°C is obtained, which corresponds to 97.5% of the theoretical yield.

TRINITRO DERIVATIVES OF CHLOROBENZENE

Of the trimtro derivatives of chlorobenzene, l-chloro-2,4,6-nitrobenzene (m. p. 81.5-83°C), known also as picryl chloride, is the most important. Next in importance is 1-chloro-2,4,5-trinitrobenzene (m. p. 116°C):





picryl chloride

l-Chloro-2,4,6-trinitrobenzene (picryl chloride) was obtained by Pisani in 1854, in the reaction of phosphorus pentachloride with picric acid. Similarly Ullmann [25] prepared picryl chloride when treating picric acid with toluene-p-sulphonchloride.

Both methods are merely of theoretical interest. A method reported by R. Boyer. Spencer and Wright [26] is of greater practical importance. It is based on the reaction of pyridine picrate with phosgene in which picryl chloride forms in theoretical yield. The pyridine in the aqueous solution left after picryl chloride has been separated is regenerated as picrate by treating the solution with picric acid. The picrate is returned to the process. According to T. Urbanski, Kuboszek and Dworak [26a] phosgene can be replaced by thionyl chloride. For industrial practice a method was developed at Griesheim [12] consisting in the nitration of l-chloro-2,4-dinitrobenzene. It was applied in Germany during World War I.

As Desvergnes [18] reports, nitration by this method was effected in the following way: 100 parts of chlorodinitrobenzene were dissolved in 200 parts of 40% oleum. A mixture of 400 parts of anhydrous sulphuric acid and 300 parts of 94% nitric acid was added to the solution. The whole was heated to 150°C with stirring, this temperature being maintained for 3 hr longer. After cooling the mixture was left for crystallization, filtered and the product was washed with cold water.

According to Desvergnes [18] and Frankland and F. H. Garner [24], chlorodinitrobenzene can be nitrated with a mixture containing less nitric acid and more sulphuric acid. The resultant product is of higher purity and the yield is also higher.

Desvergnes suggests a mixture of 560 parts of sulphuric acid (100%) and 150 parts of nitric acid (93%) for the nitration of 100 parts of chlorodinitrobenzene dissolved in 200 parts of 40% oleum at 150°C.

Frankland and Garner dissolved 100 parts of chlorodinitrobenzene in 750 parts of sulphuric acid (100%) and added 125 parts of nitric acid (93%) to the solution.

As Desvergnes pointed out in a comparison of the three methods the third one looks the best as can be seen from the following figures (Table 103):

TABLE 103

Method	Theoretical yield %	Melting point of the product °C
Griesheim	55	65
Desvergnes	82.5	75.8
Frankland and F. H. Garner	85	76

Physical properties. Picryl chloride is only sparingly soluble in water: at 15°C 0.0178 parts and at 100°C 0.346 parts dissolve in 100 parts of water.

On dissolution in hot water picryl chloride undergoes partial hydrolysis, picric acid being formed. Solubility data for picryl chloride in organic solvents are given in Table 104.

Kast [28] reports the specific gravity of molten and then solidified picryl chloride to be 1.76.

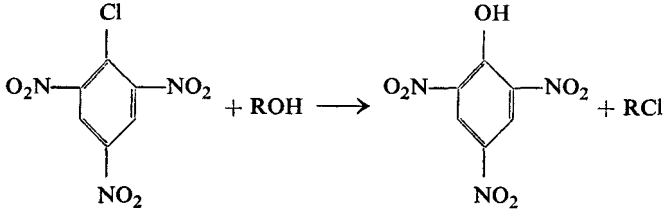
TABLE 104

SOLUBILITY OF PICRYL CHLORIDE IN ORGANIC SOLVENTS
(g/100 g OF SOLVENT)

Solvent	at 17°C	at 50°C
Methyl alcohol	10.24	34.8
Ethyl alcohol (absolute)	4.48	15.1
Ether	7.23	10.6*
Ethyl acetate	91.5	238.35
Acetone	212.0	546.4
Chloroform	12.36	233.4
Carbon tetrachloride	0.56	2.45
Benzene	36.39	428.1
Toluene	89.44	321.1

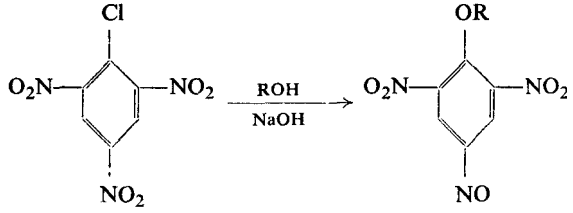
* At 31°C.

Chemical properties. The chlorine atom in a picryl chloride molecule is exceptionally reactive. Besides hydrolysis to picric acid when heated with water, as mentioned above, picryl chloride can yield picric acid when boiled with alcohols, according to the equation:



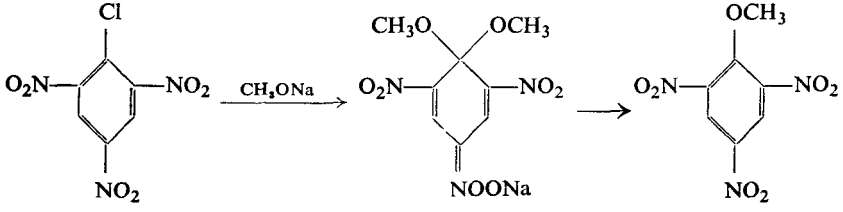
(7)

If the reaction proceeds in the presence of sodium, potassium or calcium hydroxides, the corresponding picric acid ethers are formed:



(8)

The same compounds can be obtained by the action of the corresponding alcoholates, through the formation of intermediate addition products:

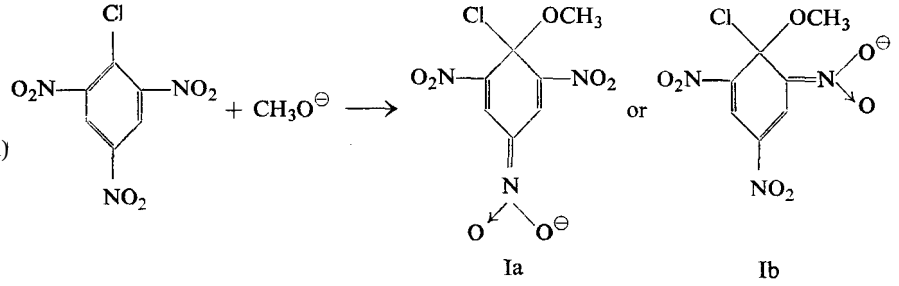


(9)

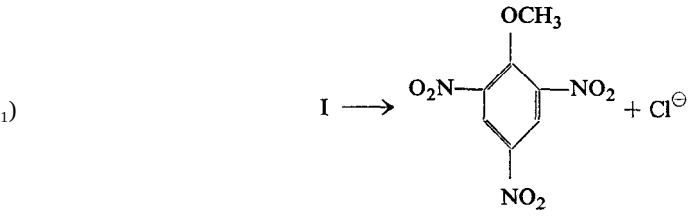
The interaction of equimolar proportions of picryl chloride gives a number of reactions, according to a recent investigation by Farmer [29]. There are two stages of the reaction. The first is very rapid and gives an intense colour. This is followed by a phase in which the red colour fades gradually. After some days the solution becomes pale yellow and yields methyl picrate (trinitroanisole). Part of the methyl picrate is formed in the first stage (ca. 40%) and the remainder in the second stage.

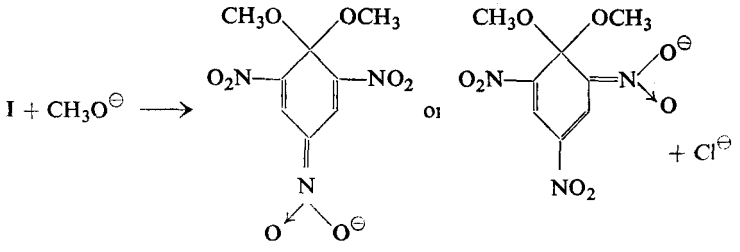
Farmer suggests the following mechanism for the reactions:

Stage I (very rapid at room temperature):

(A) 

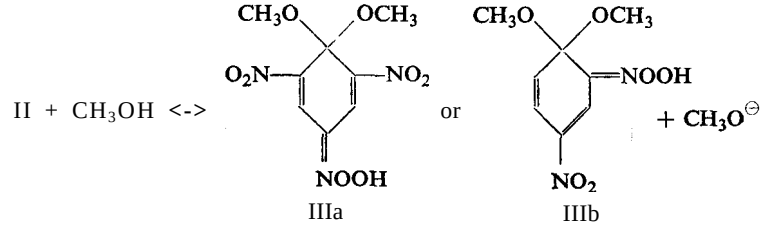
Ia Ib

(B1) 

(B2) 

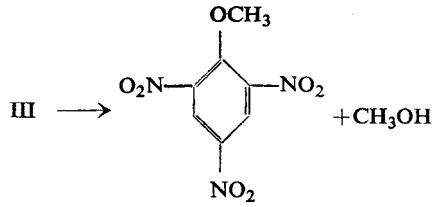
IIa IIb

Stage II - gradual conversion of the product II into methyl picrate:

(C) 

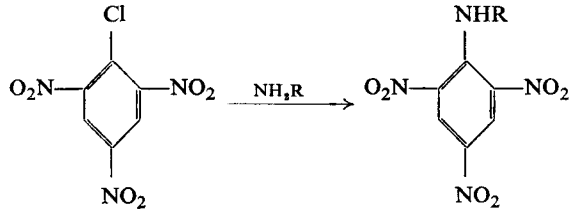
IIIa IIIb

(D_1)



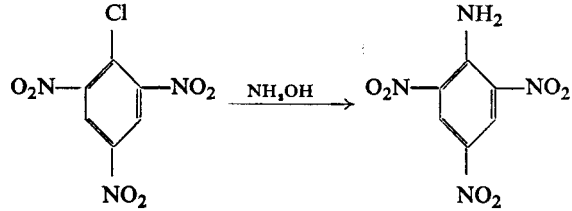
(D_2) Action of CH_3O- at very low concentration on residual picryl chloride.

With ammonia or amines picryl chloride yields picramide or its derivatives:



(10)

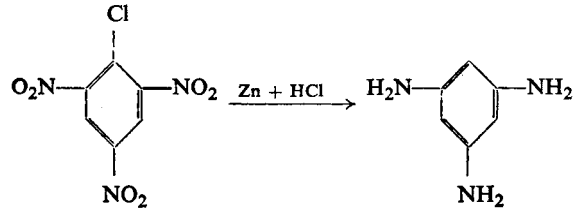
The reaction of picryl chloride with hydroxylamine hydrochloride is worth mentioning. As Borsche [24] observed, instead of the expected phenylhydroxylamine derivative, picramide was formed :



(11)

When reacted with hydroxylamine in the presence of sodium acetate, picryl chloride was found to form dinitrodinitrosobenzene (Nietzki and Dietschy [30]) (p. 258).

Picryl chloride may be used as the starting material for the preparation of trinitrobenzene (p. 255). With strong reducing agents, picryl chloride yields triaminobenzene (Fleisch [31]) :



(12)

Picryl chloride is toxic. It acts in much the same way as chlorodinitrobenzene, but is slightly less poisonous.

With aromatic hydrocarbons such as naphthalene, anthracene, acenaphthene, fluorene, phenanthrene, retene, picryl chloride forms addition compounds with the mol. ratio 1:1.

Here are a few data related to these compounds given by Jefremov [32] (Table 105).

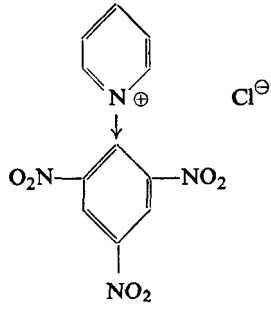
TABLE 105

Picryl chloride and the second component	m. p., °C
Acenaphthene	113.2
Anthracene	decomp.
Fluorene	64.6
Naphthalene	91.2
Phenanthrene	82.4
Retene	53.5

According to the same author (Jefremov and Frolova [32]), with l-chloro-2,4-dinitrobenzene picryl chloride forms an addition compound (mol. ratio 1:1) m. p. 31.2°C. Formerly Frankland and P. H. Garner [27] and Desvergnes [18] reported only the formation of a simple eutectic containing 44-45% picryl chloride with m. p. 25.0-25.6°C.

Recently T. Urbanski, Semenczuk and Górski [32a] confirmed the statement of Jefremov and Frolova.

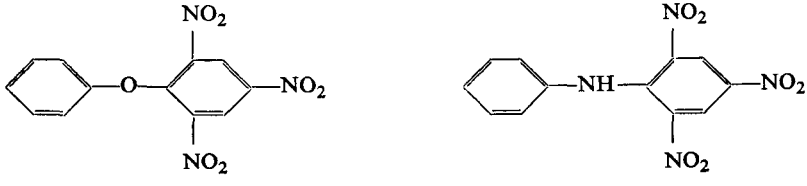
Picryl chloride reacts with pyridine to form picrylpyridinium chloride (IV)



IV (m. p. 113-115°C)

This compound, first prepared by Wedekind [33], is even more reactive than dinitrophenylpyridinium chloride (p. 454). Bielig and Reidies [23] described a reaction after Zincke and Weisspfennig's work [22] which resulted in the formation of hexanitrodiphenyl sulphide (picryl sulphide) (p. 553).

Okon [34] in a number of investigations found that when picrylpyridinium chloride reacts with phenols or aromatic amines, derivatives of trinitrodiphenyl oxide or trinitrodiphenylamine are obtained :



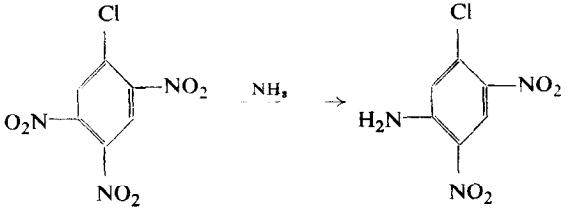
On treating picrylpyridinium chloride with alcohol Hodges [35] obtained picryl-

pyridinium picrate. The same salt was obtained by Okon when subjecting picryl-pyridinium chloride to hydrolysis by means of an aqueous solution of pyridine.

1-Chloro-2,4,5-trinitrobenzene

By the nitration of 1-chloro-3,4-dinitrobenzene with nitric acid in the presence of 40% oleum, at a temperature of 140-150°C a picryl chloride isomer, 1-chloro-2,4,5-trinitrobenzene, is formed.

A nitro group in the position ortho and para to other nitro groups exhibits higher reactivity than a chlorine atom. That is why by the action of, for example, ammonia, chlorodinitroaniline can be formed:

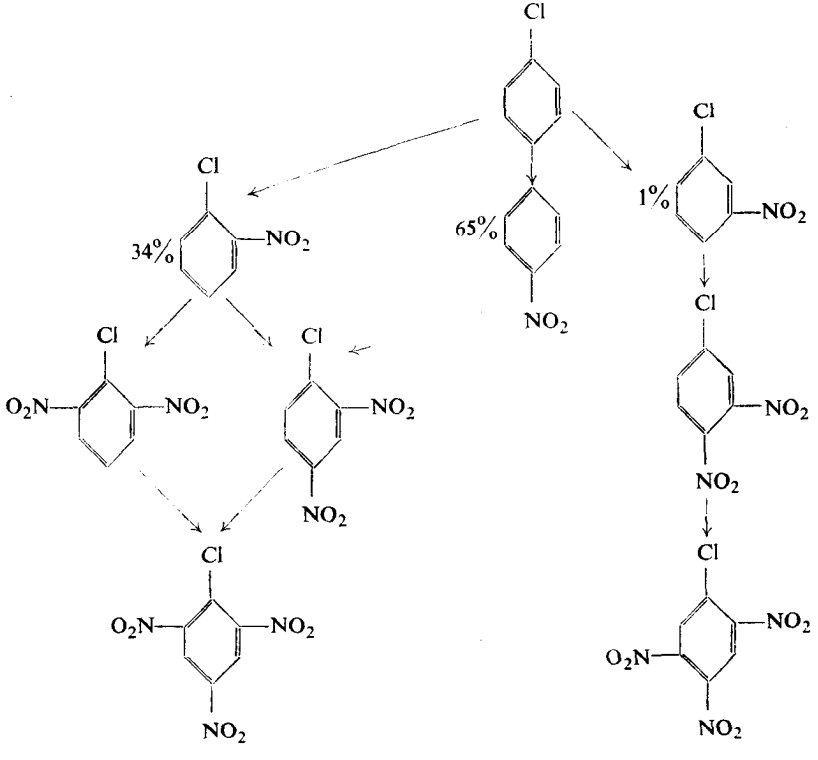


(13)

The chlorine atom in 1-chloro-2,4,5-trinitrobenzene becomes reactive only at higher temperatures.

Diagram of the nitration of chlorobenzene

The following diagram represents the complete process of nitration of chlorobenzene to trinitro derivatives :



THERMOCHEMICAL AND EXPLOSIVE PROPERTIES OF CHLORONITROBENZENES

Desvergnes has tested the explosive properties of 1-chloro-2,4-dinitrobenzene in a manometric bomb. At a density of 0.25, on comparison with other dinitro compounds, he obtained pressures:

for chlorodinitrobenzene	2016	kg/cm^2
for chlorodinitrophenol	2084	,,
for dinitrobenzene	2194	,,

It can be seen from the above that the explosive properties of chlorodinitrobenzene are slightly inferior to those of dinitrobenzene.

Experiments with chlorodinitrobenzene in mixture with picric acid for filling shells have given no satisfactory results.

NITRO DERIVATIVES OF *p*- DICHLOROBENZENE

In the explosives industry only the nitro derivatives of p-dichlorobenzene and 1,3,5-trichlorobenzene have gained any importance.

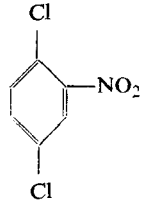
p- Dichlorobenzene is the most important of the dichlorobenzene isomers, being the principal product in the chlorination of benzene. Other isomers are formed in smaller quantities.

Mono- and di-nitro derivatives were first obtained by Jungfleisch [9] in 1868. Kijrner [36] demonstrated that the product of dinitration of *p*- dichlorobenzene consists of the α– and β– isomers. Morgan and Norman [37] isolated yet another one, the γ– isomer. The preparation and properties of all these isomers were investigated by Holleman [38].

Towards the end of World War I *p*- dichlorodinitrobenzene was used in the U.S.A for shell filling under the name of "Parazol". When brought to explosion it produced an irritating gas, because of the large quantity of chlorine in the molecule. This was probably the reason why it was used as an explosive, as its power was relatively poor.

Mononitro derivatives of *p*- dichlorobenzene

1,4-Dichloro-2-nitrobenzene (m. p. 55°C; b. p. 267°C) was obtained by Jungfleisch by the nitration of *p*- dichlorobenzene.

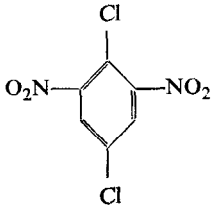


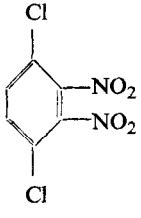
A product of higher purity was isolated by Beilstein and Kurbatov [39] from the products of chlorination of nitrobenzene in the presence of antimonium chloride

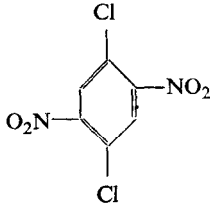
(*o*- and *m*- chloronitrobenzenes were also obtained in the reaction). The crude product contains traces of chloropicrin as an impurity.

Dinitro derivatives of *p*- dichlorobenzene

Three isomeric *p*- dichlorodinitrobenzenes α (m. p. 106°C), β (m. p. 101°C; b. p. 318°C) and γ (m, p. 119°C) are known, with the nitro groups in the positions 2,6- (3,5-), 2,3- and 2,5- (3,6-) respectively.


α


β


γ

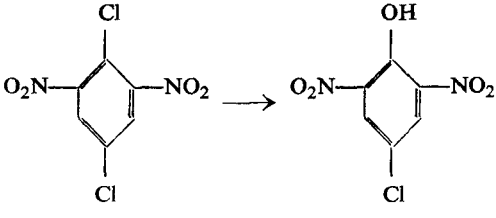
The 2,6-isomer is the principal product of nitration of *p*- dichlorobenzene, the 2,3-isomer being formed in a smaller quantity, and the 2,5-isomer to a still smaller extent.

The melting point of the crude nitration product ranges between 60°C and 80°C. Traces of chloropicrin can be detected in the product.

MacLeod, Pfund and Kilpatrick [40] believed that the 2,6- and 2,5-isomers formed an addition compound (in a 3:2 ratio), melting at 81°C. The isomers are very poisonous (Voegtlin [41]).

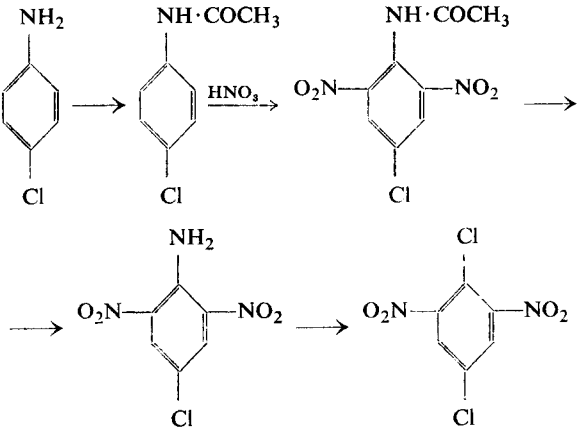
1,4-Dichloro-2,6-dinitrobenzene is difficult to dissolve in water and cold alcohol, though it dissolves readily in hot alcohol and in most organic solvents.

One of the chlorine atoms (adjacent to the nitro groups) is very reactive and can easily be substituted by some other group. In consequence, on boiling the compound with, for example, an aqueous solution of sodium carbonate, chlorodinitrophenol can be obtained:


(14)

With ammonia or amines it yields the corresponding amines, the reactions being characteristic of such chloronitro compounds.

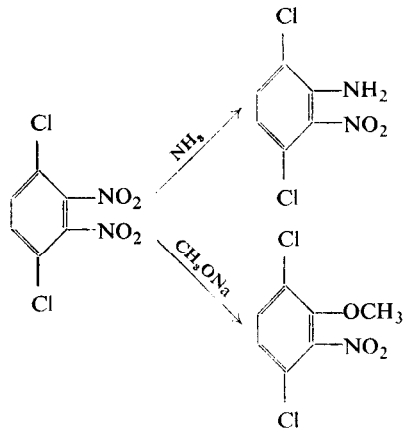
Holleman [38] obtained very pure 1,4-dichloro-2,6-dinitrobenzene in the following way:



(15)

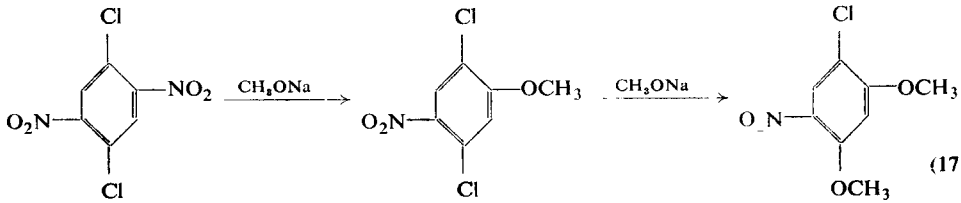
The reactivity of the nitro groups in 1,4-dichloro-2,3-dinitrobenzene and 1,4-dichloro-2,5-dinitrobenzene is exceptionally high, exceeding that of the chlorine atom.

Thus, Körner [36] observed that when treated with ammonia the dinitro-isomer having the NO_2 groups in the 2,3-positions is converted to dichloronitroanilinc. Holleman found that with sodium alcoholate the compound yielded dichloronitro-anisole :



(16)

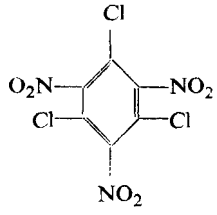
Holleman believed the 2,5-isomer behaved in the same way at the first stage of the reaction. Only by prolonged treatment with an alcoholate can a chlorine atom be substituted, a resorcinol derivative being formed:



(17)

2,4,6-TRINITRO DERIVATIVE OF 1,3,5-TRICHLOROBENZENE

1,3,5-Trichloro-2,4,6-trinitrobenzene (m. p. 187°C) can be prepared by the nitration of 1,3,5-trichlorobenzene with anhydrous nitric acid and oleum (Jackson and Wing [42]). However, according to van Ryn [43] the yield is poor.



Alone, the compound is of no interest as an explosive, for 1,3,5-trichlorobenzene is too expensive as a starting material. It is prepared by the chlorination of aniline followed by diazotization and reduction with alcohol. Nevertheless it may be used for the preparation of explosives with certain specially valuable properties, for example, an initiating substance - trinitrotriazidobenzene - (Vol. III) or for the very powerful high explosive - trinitrotrimethylnitroaminobenzene (Vol. III). It was used in Germany as an insecticide.

Manufacture of 1,3,5-trichloro-2,4,6trinitrobenzene. The I. G. Griesheim Works applied the following process for the manufacture of the above product.

The reactor is charged with 980 kg of 30% oleum to which 100 kg of solid trichlorobenzene is added during the course of one hour. The whole is heated to 100°C for another hour and kept at this temperature for 2-3 hr longer with constant stirring. Towards the end of this operation sulphonation takes place. The reaction may be considered complete when a sample of the mixture taken from the nitrator dissolves completely in water.

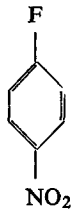
After cooling the reactor contents to 50°C 300 kg of 99% nitric acid are added during about 4 hr. While this is being done the temperature rises to 100°C. After all the nitric acid has been added, the mixture is stirred for another 10-14 hr, then during the course of a further 8 hr the temperature is gradually raised to 140-145°C. As too rapid a rise of temperature would involve the risk of decomposition, if this occurs the nitrator contents should be drained off into a safety tank. After a temperature of 140-145°C has been attained, the mixture in the nitrator is stirred at this temperature for further 45 hr. At this stage of the process the product of the reaction crystallizes. Then the nitrator contents are cooled down to 20°C and transferred by compressed air to the filter. The filtered product is transferred to a washing tank, where it is washed by mixing with cold water, followed by decantation, several times until free from acid (Congo paper test).

The spent acid contains 13% of HNO_3 and $H_2SO_4 + SO_3$ equivalent to 90% H_2SO_4.

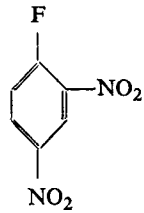
The washed, acid-free product is filtered off on a vacuum filter and dried under reduced pressure at 100°C. In this way 125 kg of the product melting at 189 -190°C are obtained, which corresponds to 72% of the theoretical yield.

NITRO DERIVATIVES OF FLUOROBENZENE

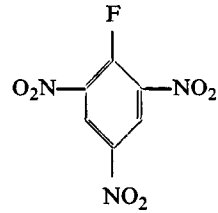
The most important nitro derivatives of fluorobenzene are:



m. p. 27°C



m. p. 25.8°C



m. p. 35°C

The nitration of fluorobenzene was studied by a number of authors. Most of the earlier work was devoted to mononitration (Wallach [44], Hollernan [45], Swarts [46]).

Dinitration to obtain 1,2,4-fluorodinitrobenzene was described by Holleman and Beekman [47] who nitrated *p*- fluoronitrobenzene. Zahn and A. Würz [48] prepared the same dinitrocompound by nitrating fluorobenzene. 1,2,4,6-Fluorotrinitrobenzene (picryl fluoride) was prepared by Olah, Pavlath, J. Kuhn and Varsanyi [49] by acting on 1,2,4-fluorodinitrobenzene with a nitrating mixture composed of fuming nitric acid and 60% oleum. The yield was 36% of theoretical.

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CHAPTER XIII

NITRO DERIVATIVES OF PHENOL

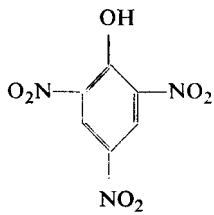
GENERAL INFORMATION

AMONG nitrophenols 2,4,6-trinitrophenol - picric acid - is of the greatest importance. The fact that this compound was first obtained as long ago as the mid-eighteenth century can be explained by the exceptional ease with which nitro groups can be introduced into the aromatic ring, due to the presence of the phenol group.

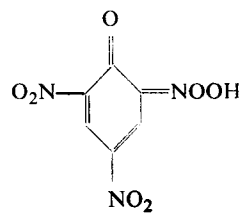
Three nitro groups can be introduced by nitrating with nitric acid of a relatively low concentration, while concentrated acid enables four and even five nitro groups to be introduced.

The presence of nitro groups enhances the acidic properties of the phenol group. This is why the trinitro derivatives are also called acids, e.g. trinitrophenol is known as picric acid and trinitroresorcinol as styphnic acid. These compounds readily form salts with metals or bases. Polynitro derivatives of phenols also form addition compounds with hydrocarbons, e.g. naphthalene.

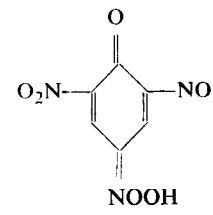
According to Hantzsch, nitrophenols exist in two forms: a phenolic, colourless form (I) and a quinonoid coloured one (IIa and IIb). This occurs with picric acid:



I



IIa



IIb

Due to the presence of a phenolic group nitrophenols are soluble in water and their acidic character enables them to dissolve in aqueous solutions of bases with the formation of the corresponding salts. Solutions of the salts are usually brightly coloured due to the presence of form II. Strong acids precipitate nitrophenols from their solutions as colourless products.

The ability of nitrophenols to appear in the coloured quinoid form has been utilized in acidimetry, where some of them are used as indicators, e.g. *m*- and *p*- nitrophenols, 2,4-, 2,6- and 2,5-dinitrophenols, nitrohydroquinone etc.

Of all the nitrophenols, picric acid has been known the longest. The first mention

of it can be found in alchemical writings of 1742, in which Glauber's experiments are described. He acted with nitric acid on wool or horn and isolated picric acid in the form of its lead or potassium salt. A more detailed description was given by Woulfe [l] in 1771, who prepared picric acid from indigo by treating it with nitric acid and found that the new substance had dyeing properties ("indigo yellow"). while Haussmann [2], in 1788, proved that it behaved like an acid. Later, many workers obtained the same product by acting with nitric acid on various organic substances, such as silk, natural resins etc. (Welter [3]; Braconnot [4]). Chevreul [5] was the first to express the opinion that picric acid contained certain constituents of nitric acid and this was later confirmed by Dumas [6] and Marchand [7]. The latter gave $C_{12}H_6N_6O_{14}$ as the empirical formula of picric acid which is exactly double the correct formula.

Some of the authors had drawn attention to the explosive character of picric acid salts, but it was not until 1830 that Welter [3] suggested the possibility of applying picrates as explosives. At that time picric acid was obtained solely by acting with nitric acid on indigo. Marchand [7] expressed the view, which proved to be true. that it was aniline, formed as an intermediate product in the process of decomposition of indigo, silk and other organic matter, which yielded picric acid under the influence of nitric acid.

The constitution of picric acid was determined by Laurent [8] in 1841. He prepared it by reacting phenol with nitric acid. He was also able to isolate dinitrophenol formed in an intermediate stage of the nitration. A further improvement in the method of preparation of picric acid from phenol was its sulphonation prior to nitration (Schmidt and Glutz [9]).

In the second half of the nineteenth century, picric acid was very widely used as a fast dye for silk and wool. The first definite suggestions as to the application of picric acid for the manufacture of explosives go back to the early second half of the nineteenth century. They referred to the application of picric acid salts as by then the explosive properties of picrates were already well known. Thus, for example, Designolle [10] suggested potassium picrate, and Brugere [11] ammonium picrate as propellants (Vol. III), while in 1871 Abel [12] proposed ammonium picrate as a high explosive. At that time potassium picrate was already being used in Great Britain and in the U.S.A. for filling shells.

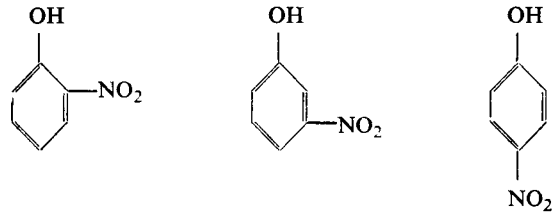
The view then prevailed, supported by such an authority as Abel, that picric acid itself is not an explosive but only its salts are. Nevertheless in 1873 Sprengel [13] proved that picric acid could be brought to explosion by a detonator and Turpin [14] proposed applying this property of picric acid by utilizing it for filling shells. In Russia methods of preparation of picric acid and using it as a shell filling were worked out near 1894 by Panpushko [15]. Eventually picric acid was accepted all over the world as the basic high explosive for military uses.

Since picric acid melts at high temperature, shells are loaded by pouring it in. mixed with various nitro compounds: dinitrophenol, mono- and di-nitronaphthalenes, TNT, TNX etc. (Vol. III).

However, after the useful properties of TNT as a material for filling shells had been established (early twentieth century), the importance of picric acid decreased somewhat. Nevertheless it was still widely used mainly because of its very simple method of preparation. In the course of time, however, as themethods of manufacture of TNT continuously improved and new sources of toluene (for example petrochemical synthetic toluene) became available, the importance of the latter went on increasing. The acidic character of picric acid and its corrosive action on metals resulting in the formation of salts sensitive to impact and friction led to a decline in the importance of picric acid, and there is a trend to eliminate it from armaments altogether. Because of its relatively high sensitiveness to impact, picric acid alone was unsuitable For filling certain special purpose ammunition, for example For armour piercing shells (p. 322).

MONONITRO DERIVATIVES OF PHENOL

Three isomeric mononitrophenols are known: *ortho* (m. p. 44-45°C; b.p. 214-216°C with decomposition); *meta* (m. p. 96°C) and *para* (m. p. 114°C):



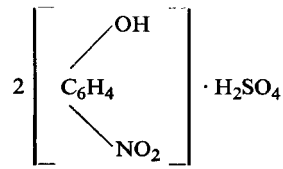
The *o*- and *p*- isomers are always formed when phenol is nitrated with dilute (e.g. 30%) nitric acid, the proportion of the *o*- isomer increasing with nitration temperature.

Separation of the two isomers may be accomplished by steam distillation: the volatile *o*- nitrophenol passes over, while the *p*- isomer remains in the residue.

Since apart from the nitrophenols some dark coloured, often resinous by-products are formed, *o*- and *p*- nitrophenols are Frequently prepared on an industrial scale From the corresponding chloronitrobenzene derivatives.

Pure *p*- nitrophenol may also be prepared by nitrosation of phenol, followed by oxidation of *p*- nitrosophenol with dilute nitric acid. The *m*- isomer is usually prepared by diazotization of *m*- nitroaniline.

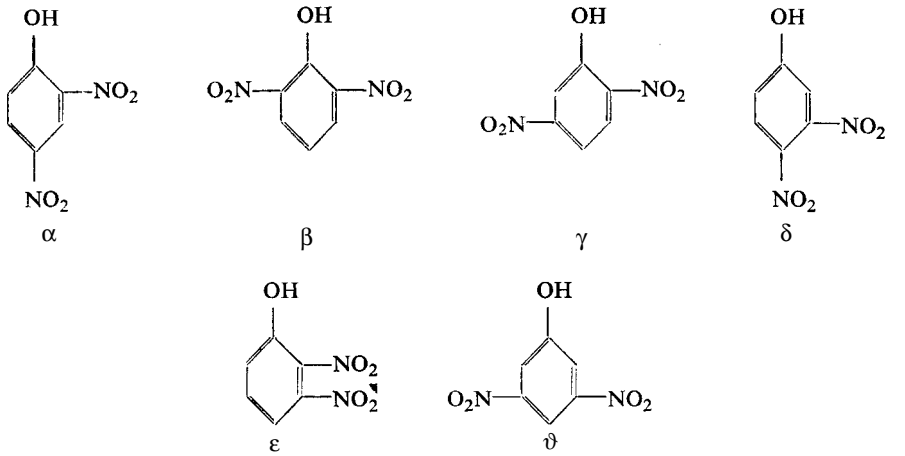
The *m*- and *p*- isomers combine with sulphuric acid to Form molecular compounds, melting at 83°C and 90°C respectively:



while *o*- nitrophenol does not yield such a compound (Kendall and Carpenter [16]).

DINITRO DERIVATIVES OF PHENOL

There are six isomers of dinitrophenol: α or 2,4- (m. p. 113-114°C), β or 2,6- (m. p. 62-63°C), γ or 2,5- (m. p. 104-108°C), δ or 3,4- (m. p. 134°C), ε or 2,3- (m. p. 114°C) and ϑ or 3,5- (m. p. 122°C).



Of these only the 2,4-isomer is used in explosive compositions or as a starting material for the preparation of picric acid by one of the methods described later. The 2,6-isomer on nitration also gives picric acid but it is not used for this purpose on a commercial scale. Both these isomers may be obtained by the nitration of phenol with nitric acid. All the other isomers are prepared by indirect methods.

Laurent [8] was the first to obtain dinitrophenol by nitrating phenol. Investigations that followed revealed that Laurent's dinitrophenol was not a chemical individual, but a mixture of the 2,4- and 2,6-isomers. Kiirner [17] obtained pure 2,4-dinitrophenol by the nitration of *p*- nitrophenol and Armstrong [18] prepared 2,6-dinitrophenol along with some 2,4-isomer, starting from *o*- nitrophenol. Clemm [19] determined the constitution of 2,4-dinitrophenol, which was later confirmed by Salkowski [20].

Finally Hübner and W. Schneider [21] defined the conditions under which the formation of the two isomeric dinitrophenols must proceed and pointed out the difference in their structures. They proved the *p*- nitrophenol was nitrated to 2,4-dinitrophenol when using 54% nitric acid. *o*- Nitrophenol is slightly more difficult to nitrate and yields a mixture of 2,6- and 2,4-dinitrophenols. The two isomers may be separated by steam distillation, since the 2,4- is more volatile than the 2,6-isomer. In consequence the residue in the retort becomes enriched in the 2,6-isomer which can finally be obtained in a pure form. Another method of separation is based on taking advantage of the difference in solubility of the barium salts of the two isomers, the 2,4-isomer salt being readily soluble in water, while the salt of the 2,6-isomer dissolves only with difficulty.

TABLE 108

CHARACTERISTICS OF 2,4-DINITROPHENATES

Salt	Number of molecules of water of crystallization	Dehydration temperature °C	Initiation temperature °C	Inflammability from flame
NH_4	1	50*	-	
Na	1	180	380	readily inflammable
Mg	12, 9, 1	180	-	
K	1,½	160	400	
Ca		180	-	
Mn	5	50* (monohydrate)	340	
Ni	8	100*	-	
Cu	-	-	340	
Zn	-	50*	355	
Sr	3	150	-	
Ba	6, 5, 4	160-180	-	
Hg	-	50	355	highly inflammable
Pb	6	15**	345	

* At 38 mm Hg.
** At 10 mm Hg.

In 1930 Desvergnes [25] gave the following values for the solubility of the barium salt in water and alcohol:

in 100 ml of water at	25°C	1.5 g
	75°C	7.2 ,,
in 100 ml of alcohol it	22°C	0.3 ,,
,, ,, ,, ,, ,, ,,	78°C	3.5 ,,

Apart from this barium dinitrophenate dissolves easily in acetone, whereas it is insoluble in chloroform and ether.

TOXICITY OF DINITROPHENOLS

Dinitrophenols are highly toxic. According to Mayer [30], 2,4-dinitrophenol is toxic not only when ingested but also when its dust is inhaled or absorbed through the skin. Fatal cases are known which were caused by inhalation of dust in a concentration of 0.004 mg/l. A dose of 0.01 g/kg of body weight is considered toxic. Other authors report 0.2 g/kg as the fatal dose, pointing out that dinitrophenol vapours in a concentration corresponding to volatility at room temperature are not poisonous.

Dinitrophenol enhances metabolism and has been applied as an agent For the treatment of obesity. Chronic dinitrophenol poisoning may cause liver and kidney damage. According to Lazarev [31], poisoning by dinitrophenol is characterized by the following symptoms: general weakness, lack of appetite, rush of blood to

the head, accelerated pulse (100-130), and respiration, a rise in temperature to 39-40°C, and moreover, in severe cases, blue mucous membranes, and spasms. Death, as *post mortem* examinations have indicated, is usually caused by pneumonia and meningitis. In many cases chronic poisoning may manifest itself by cataracts of the eye lenses, and eczema in people with sensitive skin. Inflammation of the lymphatic glands and degeneration of nails can often be observed.

Martin [32] found that dinitrophenol undergoes in the body a partial reduction either to 2-amino-4-nitrophenol or to 4-amino-2-nitrophenol and 2,4-diaminophenol. Part of the compound is excreted unchanged in the urine.

During the 1914-1918 war, in France, where dinitrophenol was manufactured in large quantities for explosive compositions, cases of poisoning among the workers, including fatal cases, were frequent, e.g. within 3 months 277 fatal cases occurred in a factory with a relatively large scale of production. Experience has shown that most of the cases are caused by impure dinitrophenol. The reason for this is, however, not clear since the impurities commonly present in the product are less poisonous than 2,4-dinitrophenol itself.

Workers in the dinitrophenol plant should be protected in the usual way (i.e. gloves, respirators, change of clothes, bath, etc.). Selection of workers handling dinitrophenol is also recommended since it has been shown that a great many people are resistant to its toxic effects, Selection is based on 15 days' medical observation of each new worker in the dinitrophenol plant, in particular in the analysis of the urine every other day. A test for the presence of aminonitrophenols is particularly importance. Usually Derrien's reaction [33] is used. According to Lazarev [31], the reaction comprises acidification of the urine with 10% sulphuric acid and diazotization with sodium nitrite, followed by shaking up the prepared solution with an ammoniacal solution of β– naphthol. If a red colour appears it indicates the presence of 4-amino-2-nitrophenol in the urine, while a violet shade is evidence for the presence of 2-amino-4-nitrophenol.

If Derrien's test is positive, the worker should be examined every day. If after 5-6 days the reaction is still positive, the worker must be barred from handling dinitrophenol. If the test is negative for 15 days or becomes negative by the end of this period, the worker may carry on with his job. Medical examination should be repeated from time to time.

In the U.S.S.R. industrial hygiene in dinitrophenol plants is determined by NKT regulation No. 211, dated 16. June 1930 and also by the U.S.S.R. Ministry of Health, Instruction No. 443, dated 17. June 1949. The regulations apply chiefly to the safe handling of dinitrophenol when used as a material for impregnating railway sleepers.

PRINCIPLES OF PREPARATION OF NITROPHENOLS

There are several methods of nitrophenol preparation:

(1) nitration of phenols;

(2) hydrolysis of chloronitro derivatives of aromatic compounds;

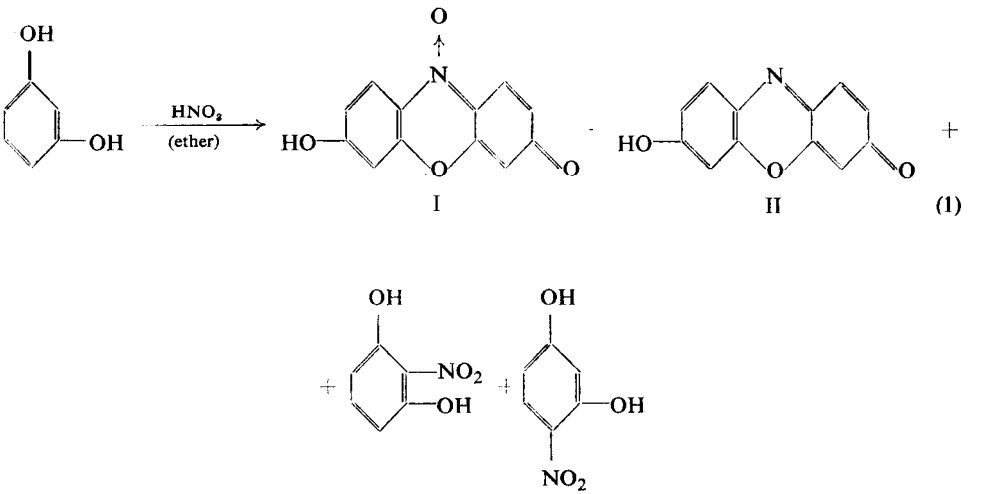
(3) oxidation of nitrosophenols;
(4) nitration of benzene or other aromatic hydrocarbons with nitric acid in the presence of mercury salts (Wolffenstein and Bötters's [23] method, pp. 110, 520)

In industrial practice methods (1) to (3) are applied, the choice depending on the product which is to be prepared, on economic considerations, etc.

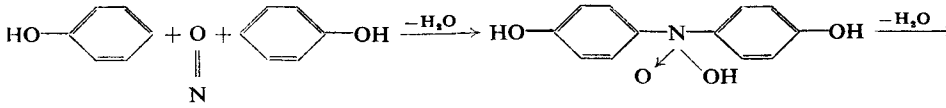
Nitration of phenol. The process is effected in two stages. The first is the sulphonation of the phenol, followed by acting with nitric acid on a solution of phenolsulphonic acid in sulphuric acid. In the latter process the sulpho groups are replaced by nitro groups (p. 501). This indirect procedure has to be adopted because the direct action of nitric acid on phenol yields undesirable by-products, sometimes brightly coloured, which contaminate the principal product.

The reaction of substitution of the sulpho groups by nitro groups should be absolutely complete. If not, the nitrophenolsulphonic acids which, due to the presence of one or more sulpho groups, are water soluble, will remainin the spent acid and in the washings from nitrophenol purification.

The direct action of nitric acid on phenol has been the subject of investigation by a number of workers. Thus, Wesselsky [34] succeeded in isolating a dark coloured substance by treating resorcinol in ether solution with fuming nitric acid. Brunner and Kramer [35] assumed that the following products, having a phenoxazine ring, were formed: resazurin (I) and resorufin (II) along with nitro derivatives of resorcinol :



The reaction of nitric acid with phenols (including resorcinol) has been fully investigated by K. H. Meyer and Elbers [36]. They isolated a reddish-brown product to which they assigned the indophenol N-oxide structure (III). The compound can be, formed directly from phenol and nitric acid, according to the scheme:



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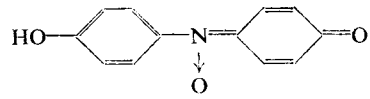
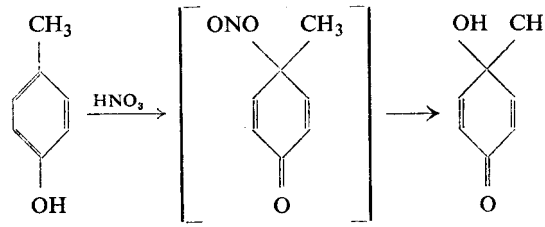


III

The direct formation of styphnic acid from resorcinol and nitric acid may also be explained by this series of reactions.

Earlier, Auwers [37] expressed the opinion that phenols when reacted with nitric acid, could yield dark coloured quinols, e.g.:



"Nitroketone"

(3)

Hydrolysis of chloronitro compounds. The chlorine atom in chlorobenzene and in its homologues becomes reactive after one or more nitro groups have been introduced into the ring. This is used widely in the preparation of nitrophenols and their ethers. The preparation of dinitrophenol, dinitroanisole and dinitrophenetole may serve as a classical example (see Chapter XVI).

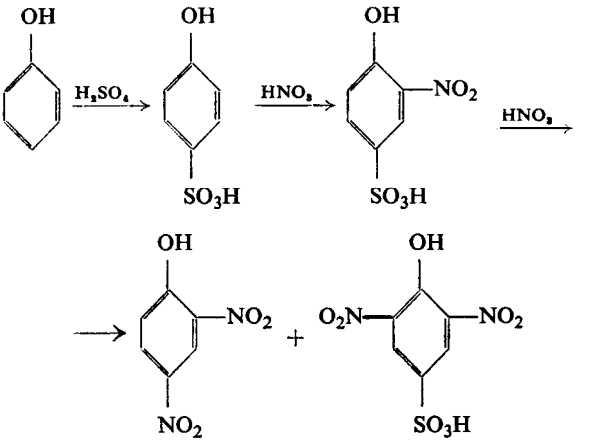
Oxidation of nitrosophenols. This method is applied when fewer nitro groups are to be introduced on the ring than those obtained by way of nitration. It is also applied when a pure product, free from its isomers, is to be prepared, e.g. *p*- nitrophenol from phenol. Direct nitration of phenol yields a mixture of the *o*- and *p*- isomers, dinitrophenol being readily formed as a by-product. Similarly dinitroresorcinol may be obtained by oxidation of dinitrosoresorcinol (p. 537).

MANUFACTURE OF DINITROPHENOL BY DIRECT NITRATION

Reverdin and de la Harpe's method [22]

This method consists in the sulphonation of phenol to phenolsulphonic acid which, on heating with nitric acid, is converted into dinitrophenol. In addition some 2,6-dinitrophenolsulphonic acid is also formed. As the latter remains in solution the yield of dinitrophenol is lower than the calculated one.

According to Marqueyrol and Lorriette [38], the reaction proceeds as follows:



(4)

100 parts of phenol are added to 400 parts of sulphuric acid (sp. gr. 1.84) heated to 110°C, then the whole is heated for 3 hr to bring it to a temperature of 130-140°C. The solution is then cooled to room temperature and 1375 parts of nitric acid (sp. gr. 1.20) are added gradually, the temperature being maintained at 45-50°C.

The mixture is left at room temperature for 24 hr, then heated gradually to about 90°C. After cooling, 2,4-dinitrophenol is filtered off, dinitrophenolsulphonic and picric acids remaining in the filtrate.

Seyewetz's method [38a]

Two modifications of this method are known. In one of them, applied at the St. Fons Factory in France, between 1915-1918, sodium nitrate is used for the nitration of phenol, and the other method utilizes dilute nitric acid.

Nitration with sodium nitrate is effected as follows. To a stoneware vessel, sodium nitrate (195 kg), water (300 kg) and sulphuric acid of sp. gr. 1.84 (240 kg) are added successively. The temperature rise brought about by mixing the sulphuric acid with water results in the complete dissolution of sodium nitrate. After all the reactants have been introduced, the temperature of the solution is about 53°C. This is the temperature required for the initiation of the nitration reaction. If the temperature is lower, it should be raised to 53°C by introducing live steam.

A solution of 25 kg of phenol in 40 kg of water heated to 26°C is poured in which takes about 4 min. During this period the temperature should not be allowed to exceed 80°C. If it does some cold water should be added. For the first 15-20 min the reaction proceeds rather violently. It is accompanied by the evolution of large quantities of nitrogen oxides.

After 60-75 min, when nitration has come to an end, water should be added to bring the temperature down to 70°C and to reduce the solubility of dinitrophenol in the spent acid.

The dinitrophenol rises to the surface of the liquid and may be skimmed off by means of a small aluminium sieve. It is then washed in wooden vats and separated on a vacuum filter.

From 100 kg of phenol 140 kg of the dark red product is obtained, which is 76% of the theoretical yield. The crude product melts at 102-103°C.

Another modification of the Seyewetz method (applied also at St. Forts 1915-18) is to use dilute nitric acid for the nitration, the process being carried out as follows. A vessel of acid resistant bricks (2 m^3 capacity) is charged with 1500 kg of 26% nitric acid (6 moles) heated to 20-30°C. An emulsion of 100 kg of phenol and 50 kg of water heated to 55-60°C is then introduced into the acid, which takes about 8-10 min.

While this is being done and during the next operations the nitrator contents are agitated by compressed air which enters through 4 pipes. During the mixing of the reactants the temperature rises to 60°C and, after 15 min from the beginning of the reaction, to 80°C. Should it rise higher than this, cold water must be added and the flow of compressed air stopped until the temperature falls again to 80°C. When it has stopped rising, i.e. when nitration has been completed, which usually requires 45 min, air is blown through the reaction mixture until the temperature goes down to 40°C. This takes about 12 hr. The dinitrophenol formed is either skimmed off from the surface of the mixture by means of a sieve or filtered off on a vacuum filter.

100 kg of phenol yields 155 kg of yellowish-orange coloured dinitrophenol, which equals 80% of the theoretical yield. The melting point of the product ranges between 101.5° and 105°C.

Nitration by this method has also been carried out in nitrators of smaller capacity for batches of 18 kg of phenol and 155 kg of 26% nitric acid. Here the temperature may be allowed to rise to 90-92°C. The yield and the purity of the product obtained are as in the above processes.

The spent acid separated from dinitrophenol contains:

HNO_3	11-12%
HNO_2	0.02-0.03%
oxalic acid	1.5%
dinitrophenol	0.4-0.5%

It is used as a spray in towers for the recovery of the nitrogen oxides evolving during the nitration of phenol to dinitrophenol. As a result of this operation the HNO_3 content in the acid rises to 19-20%.

A part of this acid is mixed with concentrated nitric acid (sp. gr. 1.40-1.50) to obtain the 26% acid to be used for nitration again. The rest is transferred to a distillation unit for concentration.

Purification of dinitrophenol

The product prepared by the above methods usually contains:

2,4-dinitiophenol	88-89%
2,6-dinitrophenol	3 4 %
p- nitrophenol	0-4%
picric acid	3-5%

Since liquid impurities may produce exudates in explosive compositions, to avoid this the crude product should be purified. For a preliminary washing, a dilute (2%) solution of sodium carbonate may be used. Picric acid reacts with the carbonate which then goes into solutions as sodium picrate. Instead of sodium carbonate milk of lime or calcium hydrogen carbonate may be used.

Desvergnes describes the purification process used in various plants as follows. A wooden double-bottomed vat of 650 1. capacity is charged with 350 kg of dinitrophenol, which is stirred with 200 1. of a 3% solution of calcium hydrogen carbonate at a temperature of 70°C. The contents of the vat are allowed to remain at rest for 1 hr, then the aqueous solution is decanted and the operation is repeated with a fresh solution of calcium hydrogen carbonate. Then the purified product is washed with cold water. The melting point of dinitrophenol obtained is about 105.5%

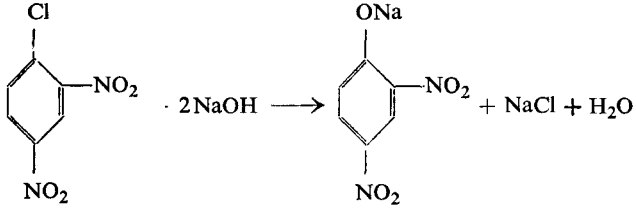
A product of still higher purity may be prepared by washing with sulphuric acid. 100 parts of dinitrophenol and 120 parts of sulphuric acid (sp. gr. 1.84) are agitated for 12 hr at room temperature. Then the sulphuric acid is filtered off and the dinitrophenol is washed with a small quantity of fresh sulphuric acid and finally several times with water. In this way the melting point of the product can be raised to 108.5°C.

The compounds dissolved both in the spent calcium hydrogen carbonate solutions and in the sulphuric acid, such as mononitrophenols, dinitrophenols and picric acid, may be recovered by precipitation: from the calcium hydrogen carbonate solution by acidification, and from sulphuric acid solution by dilution with water.

The product thus obtained may be blended with dinitrophenol for the preparation of picric acid.

MANUFACTURE OF DINITROPHENOL BY CHLORODINITROBENZENE HYDROLYSIS

In industrial practice, hydrolysis of chlorodinitrobenzene is now the main method of producing dinitrophenol. The reaction proceeds as follows:



(5)

From the resulting dinitrophenate, dinitrophenol is obtained by acidification.

Russian method

The following method (after Lebedev [39]) was applied in Russia (1915-1916) and later in the U.S.S.R.

The hydrolysis process is effected in a wrought iron reactor of 4 m^3 capacity, equipped with a cooling jacket, a heating coil and a stirrer. The reactor is charged with water heated to 70°C then a 42% solution of NaOH is run in from a measuring tank in such a quantity as to obtain 2130 1. of a 7% NaOH solution (5% in excess of the calculated quantity). Then 360 kg of molten chlorodinitrobenzene at a temperature of 70-75°C is added over a period of 10 min. The temperature rises to 100°C. When the vigorous stage of the reaction has subsided the mixture is heated to 100-110°C for 1 hr.

Towards the end of this operation a sample should be taken and diluted with water to test whether hydrolysis is complete. A completely hydrolysed product will go into solution. Otherwise chlorodinitrobenzene will collect as an oil.

According to Lebedev, the hydrolysis process requires 2 hr 20 min, including the following schedule of operations:

charging with water	15 min
charging with sodium hydroxide solution	10
analysis of the solution	10
introducing chlorodinitrobenzene	10
heating at 100-110°C	60
analysis	10
pumping out the reactor contents	15
blowing out the pipes	10
Total	2hr20min

As a result of the hydrolysis process a sodium dinitrophenate solution is formed. To obtain'dinitrophenol this solution is transferred to a wooden vat containing 30% sulphuric acid in a quantity exceeding the calculated amount by 5%. Spent acid from the nitration, diluted with water to the required concentration, may be used.

After testing the suspension for complete acidification (with Congo red test paper), it is transferred by compressed air, while still hot (70°C), to a cloth-lined vacuum filter. The dinitrophenol is washed on the filter 3-4 times with water until the acid content in the washings is reduced to 0.01%. Then it is centrifuged in copper centrifuges to a moisture content of 12-15%.

According to Lebedev, the time required for the conversion of dinitrophenate to dinitrophenol is 60 min individual operations requiring:

charging the reactor with acid	10 min
introducing the dinitrophenate	15
stirring	15
analysis	10
draining off on the filter	10
Total	60 min

The product is then dried to reduce the moisture content to 1-2%.

From 100 kg of chlorodinitrobenzene roughly 82 kg of dinitrophenol is obtained, the yield being 91% of the theoretical.

German method.

The German process of hydrolysis (applied at Griesheim) comprises the following operations :

1300 kg of chlorodinitrobenzene and 7500 1. of water (90°C) are charged into the reactor. To this mixture, 1500 kg of a 35% solution of NaOH is introduced with stirring over a period of 4 hr, the temperature being maintained within 95-100°C. If a test for a complete hydrolysis is satisfactory, the solution is introduced with stirring to about 780 l. of hydrochloric acid (30%). The mixture is then cooled to 30°C and the separated dinitrophenol is filtered off on a vacuum filter, washed with cold water, dried and ground.

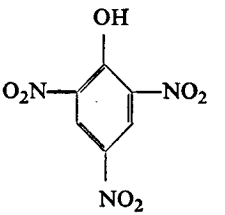
Dry dinitrophenol prepared by hydrolysis of chlorodinitrobenzene usually melts at 110-111°C. Its impurities come from the chlorodinitrobenzene, which may contain unhydrolysed admixtures (such as *m*- chloronitrobenzene, dichlorodinitrobenzene isomers, *m*- dinitrobenzene).

Dinitrophenol from chlorodinitrobenzene, to be used for the preparation of picric acid, should satisfy the following specifications (Lebedev [39])

melting point (determined as setting point)	not below 109°C
inorganic matter (ash)	max. 0.2%
iron content in ash	trace
lead content in ash	none
dinitrophenates and picrates	none
acid content (calculated on H_2SO_4)	no more than 0.1%
metal chlorides	no more than 0.5%
chlorodinitrobenzene	no more than 0.5%
dinitrophenol	not less than 96%

PICRIC ACID

Picric acid is the most important of the trinitro derivatives of phenol. The commercial product for military purposes is 2,4,6-trinitrophenol of high purity:



As an explosive it is known under various names: Ekrasit (Austria), Mélinite (France), Granatfiillung 1888-abbrev. Grf 88 (for shells), Sprengkörper 88 (for field engineer cartridges) (Germany), Pertite (Italy), Shimoza (Japan), TNF (Poland), Picrinit (Spain), Lyddit (United Kingdom), Melinit (U.S.S.R.).

PHYSICAL PROPERTIES

Picric acid crystallizes in colourless or yellowish needles or lamellae of the orthorhombic-bipyramidal system. The melting point of picric acid is 122.5°C and its

setting point 121.3°C Kast [40]). When heated to a temperature above its melting point it begins to sublime.

Specifications for commercial picric acid differ in various countries but the setting point should never be lower than 120°C.

Solubilty. Doliriski [41] gave the following figures for the solubility of picric acid in water at various temperatures (Table 109) (see also Findlay [41a]).

TABLE 109

SOLUBILITY OF PICRIC ACID IN WATER

Temperature °C	Content of picric acid, g	
	in 100 g of the solution	in 100 g of the solvent
0	0.67	0.68
10	0.80	0.81
20	1.10	1.11
30	1.38	1.40
40	1.75	1.78
50	2.15	2.19
60	2.77	2.81
70	3.35	3.47
80	4.22	4.41
90	5.44	5.72
100	6.75	7.24

The solubility of picric acid in sulphuric acid varies with the concentration of the latter. It is highest for concentrated acid and lowest in 18-20% acid. This can be seen from Table 110 [41b].

TABLE 110

SOLUBILITY OF PICRIC ACID IN H_2SO_4

H_2SO_4 CONCENTRATION %	PICRIC ACID CONTENT IN 100 G OF THE SOLUTION		
	18°C	50°C	80°C
0	1.184	2.399	4.541
2.3	0.230	0.692	1.940
4.7	0.142	0.368	1.251
10.0	0.091	0.265	0.727
18.0	0.079	0.214	0.561
25.5	0.092	0.230	0.587
50.5	0.429	0.645	1.104
69.7	0.928	1.424	2.203
87.9	2.461	5.826	7.610
97.4	7.531	12.785	24.020
100.0	10.180	16.230	25.860

In Table 111 data for the solubility of picric acid in dilute nitric acid at 25°C are given.

TABLE 111

SOLUBILITY OF PICRIC ACID IN NITRIC ACID (DRUCKER [42])

HNO_3 concentration mole/l.	Picric acid concentration mole/l.
0.00000	0.05327
0.00635	0.05095
0.02564	0.04281
0.05166	0.03493
0.0872	0.02604

In organic solvents picric acid dissolves more readily than in water as Table 112 shows.

TABLE 112

SOLUBILITY OF PICRIC ACID IN ORGANIC SOLVENTS

Solvent	Temperature °C	Amount of the solvent	Amount of picric acid
Ethyl alcohol	25	100 parts	7.452 parts
Ethyl ether	13	100 „	1.08 „
Ethyl ether (water saturated)	13	100 „	4.00 „
Benzene	6	100 „	3.50 „
Benzene	15	100	5.9 „
Toluene	20	100 ml solution	12.0 g
Amyl alcohol	20	100 „ „	1.755 g

The solubility of picric acid in aqueous solutions of methyl-, ethyl-, isopropyl- and n-propyl alcohols, as well as of acetone has also been determined (Duff and Bills [43]), Table 113.

TABLE 113

SOLUBILITY OF PICRIC ACID IN AQUEOUS SOLUTIONS OF ORGANIC SOLVENTS

Percentage of the organic component of the solution	Grammes of picric acid per 100 g of the solvent at 25°C		
	Methyl alcohol	Ethyl alcohol	Acetone
0	1.3	1.3	1.3
30	2.4	3.1	9.5
60	7.1	10.5	46.7
80	-	13.8	87.8
81		13.8	-
85	-	13.2	
90	16.0	12.3	
100	21.1	8.0	43

In Table 114 partition coefficient of picric acid between two liquid phases arc tabulated for water-toluene and water-ether (Sisley [44]).

TABLE 114

PARTITION COEFFICIENTS OF PICRIC ACID BETWEEN TWO LIQUID PHASES

Concentration of picric acid g/l. of the solution	Solution volumes water-toluene	Grammes of picric acid in 100 ml of the solution		Partition coefficient
		water	toluene	
10g	100 : 100	0.275	0.725	1 : 2.63
3		0.125	0.175	1 : 1.24
1		0.062	0.038	1 : 0.63
0.1		0.010	-	-
-	water-ether	water	ether	-
10g	106 : 96	0.374 -	0.670	1 : 1.79
1		0.085	0.011	1 : 0.129
0.1		0.0105	0.00011	1 : 0.010
0.01		0.000952	-	-

Similar values have been obtained by Sisley for amyl alcohol and water.

Mindowicz [45] has also studied the partition coefficient (k) of picric acid between water and various organic solvents. Table 115 summarizes his results expressed in terms of the Nemst [46] and Shilov [47] equation

$$k = \frac{C_1^n}{C_2}$$

where n is an exponent independent on the temperature, C_1 and C_2 are concentrations.

TABLE 115

Temperature °C	Benzene-water N = 1.727 $k \times 10^2$	Temperature °C	Toluene-water n = 1.667 $k \times 10^2$	Chlorobenzene-water n = 1.674 $k \times 10^2$
10	1.563	20	1.875	2.421
30	1.892	40	2.323	2.965
50	2.275	60	2.884	3.548
70	2.673	80	3.532	4.416

As may be seen from the above data, from concentrated solutions picric acid can be extracted by an organic solvent, while in the case of dilute solutions it remains in the aqueous phase.

Hygroscopicity. Picric acid is only slightly hygroscopic. Marsh [48] found that picric acid, in contact with water-saturated air at 32°C for 48 hr absorbed 0.37% of water. If, however, the picric acid contained 0.05% of SO_3, as sulphates or

sulphuric acid, it absorbed 1.9% of water under the same conditions, while at 0.16% SO_3, ca. 5% of water was taken up.

Density. The specific gravity of picric acid is 1.813, and that of molten product 1.589 at 124°C and 1.513 at 170°C. The apparent weight of the crystalline substance is 0.9-l .0.

The density of pressed picric acid depends on the pressure applied (Dautriche [49]).

Pressure, kg/cm^2	Average density, g/cm^3
275	1.315
685	1.480
1375	1.614
2060	1.672
2750	1.714
3435	1.731
4125	1.740

Kast found the density at 4000 kg/cm^2 to be 1.63 g/cm^3 and at 4500 kg/cm^2 1.74 g/cm^3. In practice, on account of the risk involved, pressures higher than 2000 kg/cm^2 are seldom applied.

Molten picric acid solidifies, when cooled slowly, to a substance of an average density of 1.66 g/cm^3. On rapid cooling a density of 1.70 g/cm^3 may be attained (Kast [40)].

THERMOCHEMICAL PROPERTIES

The specific heat of picric acid, as measured by C. A. Taylor and Rinkenbach [50], is:

Temperature, °C	Specific heat, Cal/g
0	0.234
20	0.250
40	0.266
60	0.282
80	0.300
100	0.318
120	0.337

The heat of solidification of picric acid is, according to Gamer and Abemethy [51], 4.30 Cal/mole. Rinkenbach [52] reported it to be 4.66 Cal/mole.

Heat of combustion and heat of formation of picric acid and of other nitrophenols. The heat of combustion of picric acid at constant volume (corrected for the nitric acid formed) is 621.2 kcal/mole and the heat of formation is 63.3 kcal/mole or 276.4 kcal/kg (Gamer and Abemethy [51]).

According to other authors, the heat of formation of picric acid ranges from 46.8-50.9 kcal/mole.

Garner and Abemethy have given the following values for heats of formation of other nitrophenols:

o- nitrophenol	+63.4 kcal/mole
p- nitrophenol	+66.3 kcal/mole
2,4-dinitrophenol	+69.9 kcal/mole

Heat of nitration. The heat of conversion of phenol into picric acid has been calculated on the basis of the above data (see diagram on. p. 261):

phenol - *o*- and *p*- nitrophenol	+35.0 kcal/mole
o- and *p*- nitrophenol - 2,4-dinitrophenol	+24.5 keel/mole
2,4-dinitrophenol - picric acid	+ 12.9 keel /mole
	+72.4 kcal/mole

Heat of explosion - see below, under explosive properties.

CHEMICAL PROPERTIES

An outstanding feature of picric acid is its acidic character. It readily forms picrates (they are dealt with in a special chapter, p. 525) and esters, which are phenol ethers, e.g. trinitroanisole (p. 545), trinitrophinetole (p. 548).

Like other polynitroaromatic compounds, picric acid readily forms addition products with aromatic hydrocarbons. This behaviour is especially pronounced in picric acid. Addition compounds with phenols, aromatic ketones, acids and even with nitro compounds are also known.

Here are some of the addition compounds formed by picric acid combined with other substances in molecular proportion of 1: 1:

Second component	Melting points, °C
Anthracene	ca. 141 (non uniform melting)
Benzene	84
Fluorene	a4
Naphthalene	150
Phenol	85
Resorcinol	100
Pyrocatechol	124
Guaiacol	88.6
o- Cresol	89.8
p -Cresol	ca. 65.6 (non uniform melting)
Thymol	96.8
β -Naphthol	145.8
Triphenylcarbinol	138.5
Acetophenone	ca. 50 (non uniform melting)
Benzophenone	27 (readily dissociates)
Cinnamic acid	106.5

With *m*- cresol, picric acid forms a compound (m. p. 61.6°C) containing the two constituents in the mol. proportions of 1: 2. With salicylic aldehyde it forms two non-uniformly melting compounds in the proportions of 1: 1 (m. p. - 55°C) and 1: 2 (m. p. - 35°C). With *m*- hydroxybenzoic aldehyde, picric acid forms a series of compounds containing the constituents in proportions from 1: 1 to 1: 5, dissociating at 90°C on melting.

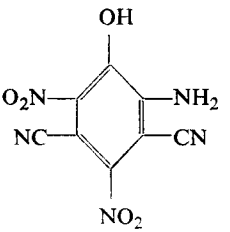
Jefremov [53] was able to identify the following compounds in molecular proportion 1: 1 by means of thermal analysis:

Constituents	M. p., °C
Picric acid with α– benzylnaphthalene	97.0
α– chloronaphthalene	125.7
α– bromonaphthalene	35.0
α– nitronaphthalene	about 55 (non uniform melting)
β– chloronaphthalene	81.5
acenaphthene	160.8
phenanthrene	132.8
retene	120.9

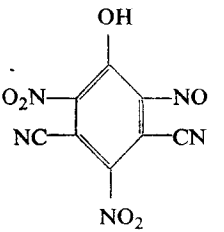
With amines, picric acid yields picrates. Some of them such as quinine or qulnoline picrates, are very difficult to dissolve in water and this may be utilized for quantitative determination of picric acid or these bases.

The composition of various practically applied eutectics given by picric acid is discussed in the chapter on fusible explosive compositions in Vol. III.

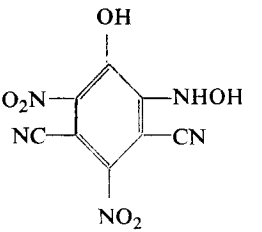
For the qualitative determination of picric acid a characteristic reaction with potassium cyanide may be utilized. When an aqueous solution of the two compounds is boiled a red-coloured potassium salt of "isopurpuric acid" is formed. Formula I was assigned to this compound by Nietzki and Petri [54], while Borsche and Böcker [55] suggested the formulae IIa or IIb.



I



IIa



IIb

However, Lobry de Bruyn [56] demonstrated that "isopurpuric acid" is a mixture of compounds in which one of the nitro groups has been reduced to an azoxy-, azo-, or nitroso group, while the cyano groups have entered the ring, replacing a hydrogen atom or a nitro group.

Picric acid is not resistant to strong oxidizing agents. It is oxidized by boiling nitric acid to yield oxalic acid. Boiling with ammonium persulphate results in a complete oxidation, according to the equation:

$$C_6H_2(NO_2)_3OH \xrightarrow{(NH_4)_2S_2O_8} CO_2 + HNO_3 + HCN \qquad (6)$$

When mildly reduced, for example with sodium sulphide or hydrosulphite or with ferrous sulphate, picric acid is converted into picramic acid, a very useful intermediate in the dyestuffs industry and a starting material for the preparation of dinitrodiazophenol, a primary explosive (Vol. III). Stronger reduction may lead to the formation of triaminophenol.

Violent boiling of picric acid with a concentrated solution of sodium hydroxide may bring about decomposition of the former:

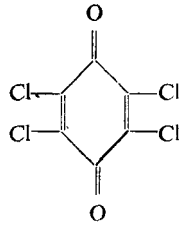
$$C_6H_2(NO_2)_3OH \xrightarrow{NaOH} NH_3 + HCN + HNO_2 \quad (7)$$

Hypochlorites decompose picric acid, which undergoes chlorination to form chloropicrin. The reaction is carried out with calcium hypochlorite. The calcium hydroxide formed in the reaction neutralizes the hydrochloric acid formed. This is a commercial method of preparation of chloropicrin.

$$C_6H_2(NO_2)_3OH + 11HOCl \xrightarrow{85^\circ C} 3\ CCl_3.NO_2 + 3CO_2 + 6H_2O + 2HCl \quad (8)$$

When reacted with chlorine, aqua regia or potassium chlorate in the presence of hydrochloric acid, picric acid yields chloranil along with chloropicrin:

$$C_6H_2(NO_2)_3OH \xrightarrow{Cl_2} CCl_3.NO_2 + \text{chloranil} \quad (9)$$



If the reaction is stopped just when the formation of chloropicrin starts. the presence of 6-chloro-2,4- and 4-chloro-2,6-dinitrophenols can be also detected along with it.

When heated to a temperature above its melting point, picric acid can react with sulphur. Addition of sulphur lowers the ignition temperature of picric acid (see below).

Action of heat. According to Kast [40], picric acid, when heated to 160°C begins to decompose slightly and an insignificant evolution of gases occurs. At 200-210°C the evolution of gases is stronger and heating at 260°C for half an hour results in explosion. The explosion may not occur below temperatures of 300-310°C when a small quantity of the acid is heated more rapidly.

Micewicz and Majkowski [54] reported that the initiation temperature of picric acid is 243-288°C on slow heating, while it rises to 337-346°C on rapid heating.

T. Urbanski and Pillich [58] found that picric acid with a 5% addition of sulphur exploded at 251°C and with 10% at 247°C whereas pure picric acid exploded at 330°C.

Picric acid melts prior to burning giving a sooty flame. The heat of fusion lowers the temperature of the layer adjacent to the burning one, so the substance may either stop burning or continue to burn only gently. In large quantities, burning of picric acid may proceed slowly, especially when it is spread over a larger area. If, however, the product is concentrated on a small area or when it is in a confined space, explosion may occur. Burning the product containing metal picrates may result in explosion. Similarly a potential danger exists when burning picric acid is in contact

with metals, since in the molten state it forms picrates which may initiate explosion. This depends largely on the metal: lead, iron, copper should be considered as particularly dangerous.

It was unexpected to find that picric acid does not decompose when exposed to sunlight. Ciamician and Silber [59] found that an alcoholic solution of picric acid when exposed to sun rays for many months does not show any change in its properties. The fact that picric acid turns slightly yellowish when exposed to light may be ascribed, according to Stepanov [60], to the formation of traces of ammonium picrate on the irradiated area.

EXPLOSIVE PROPERTIES

Picric acid decomposes according to the equation (Kast [40]):

$$16C_6H_3O(NO_2)_3 = 32CO_2 + 40CO + 4CH_4 + 2H_2O + 3C_2H_2 + 3HCN + \\ + 4.5H_2 + 21.5N_2 + 2NH_4HCO_3 + 9C \quad (10)$$

Its heat of explosion is 1000 kcal/kg, the volume of gases produced Ve = 675 l./kg and temperature t = 3230°C.

Schmidt [61] has derived a number of equations for the decomposition of picric acid at various densities. For example, at $\Delta = 1.39$ the equation derived for 1000 g (i.e. 4.36 moles) of the substance is:

$$4.36C_6H_3O(NO_2)_3 = 6.14CO_2 + 14.37CO + 3.94H_2O + 1.33H_2O + 0.16CH_4 + \\ - 0.07C_mH_n + 0.15HCN + 0.54NH_3 + 6.12N_2 + 5.1C \quad (11)$$

The heat of explosion = 960 kcal/kg, the volume of gases V_0 = 737 l./kg, t = 3530°C.

R. Robertson and Garner [62] found the heat of explosion to be 910-935 kcal/kg, and the volume of gases V. = 725 l./kg.

The impact sensitivity of picric acid is higher than that of TNT. In many countries the value of 100 has been taken for the sensitiveness of picric acid, sensitiveness of other explosives being expressed in terms of that of picric acid. Thus the value for tetryl will be 70 and that for TNT - 115-275, according to various authors.

The sensitiveness of picric acid to friction is low, but slightly higher than that of TNT.

The expansion produced in the lead block, as reported by various authors is 250-350 ml. Taking the value for TNT as 100, that for picric acid will be 102-120.

In the mortar test picric acid gives a value of 110-120, and in the sand test 104, relative to TNT = 100.

The rate of detonation of picric acid, as measured by various workers, is given in round numbers in Table 116.

TABLE 116

RATE OF DETONATION OF PICRIC ACID (m/sec)

Density	According to Kast* [70]	According to Friedrich * *[63]	According to Roth***[64]
0.7		4020	
0.9		4635	-
1.1		-	4560
1.23	-	-	5430
1.30	5980	6190	-
1.32	-	-	-
1.41	6465	-.-	6940
1.47	-	-	-
1.49	6885	-	--
1.50	7110	-	
1.54		6930	-
1.56	-	-	7504

* For unconfined charges of 21 mm diameter and a 1 g detonator.

** In a metal pipe 10-15 mm in diameter.

*** In a bakelite pipe 4.5-8.2 mm in diameter.

Cybulski [65] found the rate to be 7260 m/sec at a density of 1.7g/cm^3. As the highest rate of detonation values from 7100 to 7500 m/sec are accepted.

TOXICITY

In the unanimous opinion of a number of authors picric acid is more toxic than the nitro derivatives of toluene, xylene or naphthalene. It is, however, much less toxic than nitro derivatives of benzene.

According to Lazarev [31], the single lethal dose for a cat is 0.5 g per kg of its weight. A daily dose of 0.05-0.2 g per kg causes death after 9 days.

Saladini [66] pointed out that small doses of picric acid cause no ill-effects in man.

Koelsch [67], from observation of 1200 workers engaged in handling picric acid, described the symptoms of poisoning as follows: a yellow colouration of unprotected parts of the skin and hair, irritation of the mucous membranes and of the upper parts of the respiratory tract and the digestive tract. In addition, a constant bitter taste and a lack of appetite appear. Cases of acute or chronic poisonings were not observed.

Similar results of observations carried out at the Institute of Occupational Diseases in Leningrad were reported by Matussevich [68]. He also mentioned the nails turning yellow.

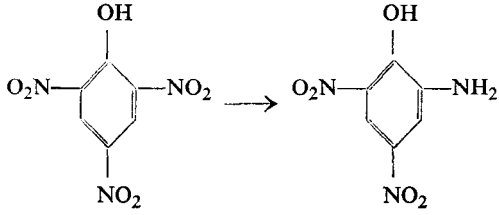
Lebedev [39] described the signs of mild poisoning by picric acid as follows: yellow coloration of the skin, the teeth, the saliva and nasal mucus, bitter taste, lack of appetite, occasionally nausea and vomiting. A decrease in the acidity of the gastric juice is also possible, as well as conjunctivities, irritation of the upper re-

spiratory tract and of the middle ear. Instances of perforation of the nasal wall are also known. In more severe cases an intense headache appears, as well as abnormally high temperature, dizziness, spasms, disturbances of the digestive organs, anaemia and more rarely kidney trouble. In women menstrual disturbances may occur. More or less severe eczema may also appear.

According to Nawrocki and his co-workers [69], a concentration of picric acid in air amounting to 1-17.5 mg/m^3 may cause severe poisoning after six hours' exposure.

Koelsch [67] suggested the following protective measures when working with picric acid. Adequate ventilation to prevent the accumulation of picric acid dust, protective clothing including gloves and head coverings to cover as large an area of the skin as possible and washing the face and the hands and rinsing the mouth before meals. Taking meals in working quarters should be forbidden. Workers should be subjected to medical inspection at regular intervals.

Karplus [70] found that in man or in animals picric acid undergoes partial conversion into the more toxic picramic acid:



(12)

According to Ishiwara [71], after a 30 min action a 0.04% aqueous solution of picric acid exhibits bactericidal activity against typhoid bacteria, staphylococci, streptococci and gonococci.

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CHAPTER XIV

MANUFACTURE OF PICRIC ACID

PRINCIPLES OF MANUFACTURE

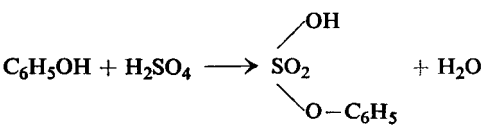
PICRIC acid is produced either by nitrating phenol or by nitrating dinitrophenol prepared by hydrolysis of chlorodinitrobenzene.

NITRATION OF PHENOL

The process is effected in two stages. Phenol is first sulphonated and then the sulphonation product is nitrated with nitric acid (p. 126).

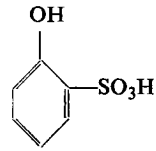
Two features of the process may justify its use. First of all, direct nitration of phenol with a nitrating mixture may lead to the formation of various by-products resulting from oxidation, condensation, resinification etc. (p. 480) which will contaminate the product and lower its yield. In addition, when two separate stages are used - sulphonation and nitration - it is possible to carry out the nitration without any excess of acids, so that the spent acids left after separation of the product may be discharged into the drainage system without further treatment which would increase production costs. This is of great importance, principally because the acids are not suitable for concentration as they contain picric acid. Picric acid is known to be rather volatile and may escape from sulphuric acid solutions if in the concentration process the H_2SO_4, content becomes higher than 72.5%. Picric acid vapours, after being condensed on metal parts of the equipment, may form picrates, for example, with lead or iron, which explode readily.

For the first stage of the process, i.e. sulphonation of phenol, sulphuric acid is used in some excess (4-4.5 moles of sulphuric acid per 1 mole of phenol). Initially a sulphuric acid ester is formed:

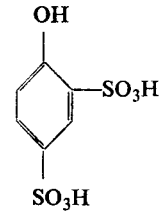


$$C_6H_5OH + H_2SO_4 \longrightarrow SO_2(OH)(O{-}C_6H_5) + H_2O \qquad (1)$$

which is later converted into a mixture of *o*- and *p*- phenolsulphonic acids:



At room temperature the conversion proceeds slowly, whereas it occurs rapidly on heating. The higher the temperature, the more *p*- isomers are formed. At 90-100°C phenoldisulphonic acid is also formed:



Its presence is advisable, as later it will facilitate the nitration process.

Marqueyrol and Loriette [1] investigated the process of phenol sulphonation with varying sulphuric acid concentration, time and temperature of sulphonation. Their results are presented below (Table 117).

TABLE 117

SULPHONATION OF PHENOL UNDER VARIOUS CONDITIONS

H_2SO_4 concentration, %		Per cent of phenol converted into disulphonic acid
92		62
93		66
94		71
96		82
97		91
100		100
Time of sulphonation with 93% H_2SO_4 at 100°C, min		
15		48
30		65
60		66
120		68
240		68.5
Sulphonation with 93% H_2SO_4, temperature °C	Sulphonation time, min	
75	30	51
75	60	59
150	15	50
150	30	66
150	60	66.5

Phenoltrisulphonic acid is formed only when using an excess of 20% oleum.

The second stage in the preparation of picric acid is the nitration of the phenolsulphonic acid obtained in the first stage of the process.

"Sulphophenol", which is the name of the starting material for the second stage, is a mixture of 1,4-phenolsulphonic and 1,2,4-phenoldisulphonic acids.

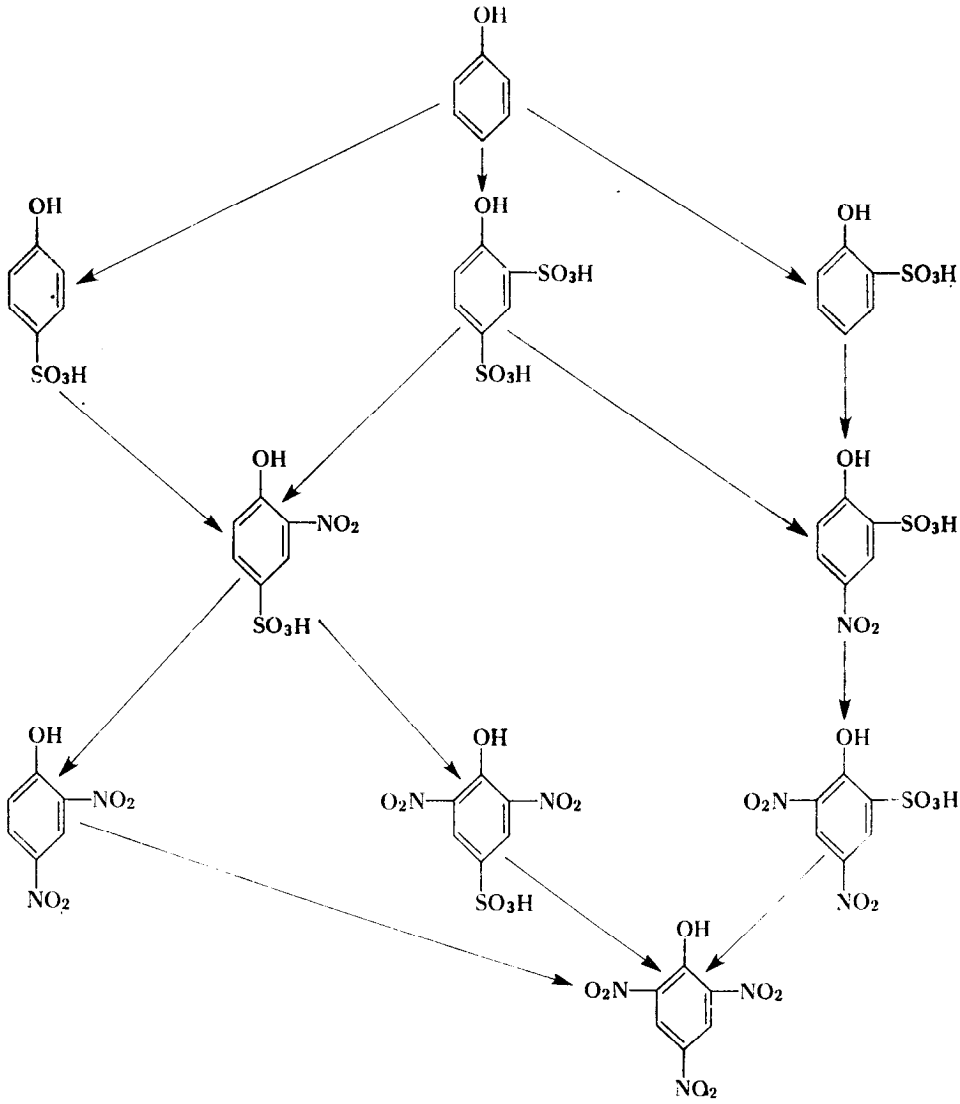
For the nitration the following nitrating agents may be used:

(a) dilute (44-65%) nitric acid;

(b) mixture of dilute nitric acid and sodium nitrate;

(c) concentrated nitric acid.

A schematic presentation of the reactions occurring in the process of preparation of picric acid acid via sulphonic acid is given below (Pascal [2]):



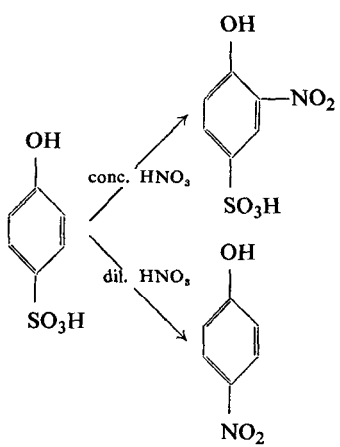
As this scheme indicates, phenolsulphonic acid is first nitrated to 2-nitro-4-sulphonic and 4-nitro-2-sulphonic acids. The former yields 2,4-dinitrophenol and 2,6-dinitro-4-sulphonic acid, and the latter 2,4-dinitro-6-sulphonic acid. All these dinitro compounds are finally converted into picric acid.

The introduction of nitro groups proceeds the more rapidly the more sulpho groups "sulphophenol" contains. The nitration of disulphonic acid is faster than the nitration of monosulphonic acid, but not so fast as the nitration of trisulphonic acid.

Thus, when heating 1-hydroxy-2,4,6-trisulphonic acid with 61% nitric acid at 110°C, picric acid is produced in a yield amounting to 90% of the theoretical (220 parts of picric acid per 100 parts of phenol), whereas from 1,2,4-phenoldisulphonic acid under analogous conditions, the yield of picric acid is 86% of the theoretical (208-210 parts of picric acid per 100 parts of phenol).

Moreover, it has been proved by Marqueyrol and Loriette [1] that the rate of formation of picric acid from 2,6-dinitro-4-sulphonic acid is higher than that from 2,4-dinitro-6-sulphonic acid. Since for the formation of both *p*- phenolsulphonic and 2,4-disulphonic acids high sulphonation temperatures are favourable, it is evident that efforts should be made to attain sulphonation temperature as high as possible. This is especially important if dilute nitric acid is to be used.

King [3] has shown that phenolsulphonic acid can be nitrated by the action of concentrated nitric acid to yield nitrophenolsulphonic acid. On the contrary, reaction with dilute nitric acid leads to the exchange of the sulphonic group by the nitro group:

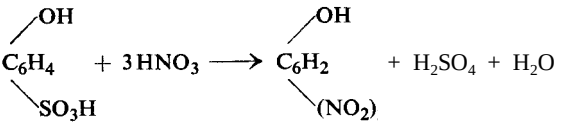


(2)

If sulphonation is carried out at a low temperature, nitric acid of higher concentration should be used or a higher temperature should be maintained during the nitration. The latter must, however, be kept within safety limits. Apart from this, higher temperatures naturally favour undesirable side reactions (e.g. oxidation).

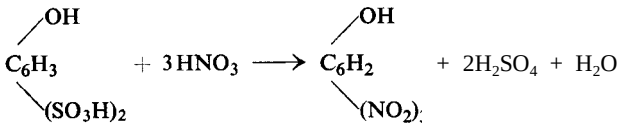
The reactions occurring in nitration with sodium nitrate are as follows:

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3 \quad (3)$$



(4)

Or



(5)

The sulphuric acid formed in reactions (4) and (5) decomposes new portions of sodium nitrate in accordance with reaction (3).

The spent acid from the nitration of phenol by the methods described contains several by-products, among them : 2,4-dinitrophenol-6-sulphonic acid in the proportions of 22 parts per 100 parts of phenol used for the process, which corresponds to a 8% loss of the phenol, and oxalic acid in the proportion of 5-6 parts per 100 parts of phenol. These are the principal by-products that lower the yield of picric acid.

A certain amount of picric acid may be converted into its salts - undesirable products - which may be formed by the contact of picric acid either with metal parts ofthe plant or with certain salts (e.g. dissolved in the water used for washing the picric acid).

The theoretical yield of picric acid amounts to 243 parts of picric acid from 100 parts of phenol. Because of by-products formation, however, the actual yield hardly exceeds 200-205 parts (82-85%) of the theoretical. During World War I in France a yield of 175 parts of picric acid (72% of the theoretical) was reported.

It should, however, be remembered that commercial picric acid prepared by this method contains lower nitrated phenols. To obtain a chemically pure product, commercial picric acid should be subjected to additional nitration (Arundal, Davies and ICI Ltd. [4]).

NITRATION OF DINITROPHENOL

This is the most modern industrial method for the preparation of picric acid from chlorobenzene via chlorodinitrobenzene (for preparation of dinitrophcnol from chlorodinitrobenzene, see p. 484). The nitration of dinitrophenol to picric acid is carried out by conventional methods, using nitrating mixtures containing some 0-5% of water.

The following three grades of purity of picric acid are specified in the U.S.S.R. standard, OST 3515 (Table 118).

TABLE 118

	Grades		
	I	II	III
General appearance	crystalline powder free from foreign matter		
Colour	light yellow		
Setting point, not less than, °C	119.5	119.5	119
Moisture and volatile matters, max.	0.5%	0.5%	0.5%
Insoluble in benzene, max.	0.2%	0.3%	1.0%
this includes :			
picrates	not present	trace	max. 0.03%
SiO_2, max.	0.05%	0.05%	0.1%
Sulphuric acid, max.	0.1%	0.2%	0.3%
Halogen	trace	trace	trace

Picric acid should be transported in wooden cases or barrels with thick walls 1.5 cm.

METHODS BASED ON PHENOL NITRATION

Raw materials. A high grade phenol should be used. The U.S.S.R. specifications of 1931, for example, require for nitration top grade phenol with a setting point not below 39°C. A small amount of moisture present, resulting in lowering the setting point to 37°C, does not prove harmful to the nitration process. The purity of the product should be tested by determining the setting point of a dry sample, which should lie within the above mentioned limits.

Nitration grade phenol should be completely soluble in water, giving a clear solution. Not more than 0.1% of non-volatile residue left after the evaporation of phenol, when heated on a steam bath, is permissible.

Acids used for the nitration of phenols should be free from any detectable quantity of lead.

NITRATION METHODS USING DILUTE NITRIC ACID OR MIXTURES OF NITRIC ACID AND SODIUM NITRATE

These are primitive methods (applied during 1914-1918 in Russia, France, Italy and Great Britain), which gained considerable popularity, solely because they enabled large scale production to be achieved rapidly by the hitherto unprepared allied powers.

The main part of the operation consisted in nitrating sulphonated phenol with materials readily available in those days - dilute nitric acid and sodium nitrate. To prevent any corrosion of the nitrators and to prevent any possible formation of metal picrates, the nitrators were built of stone-ware.

Sulphonation of phenol

The first stage of the production process - the preparation of phenolsulphonic acid - may be effected in various ways.

Pascal [2] describes it as follows. Phenol, which is supplied in iron drums, is melted by placing the drums, after removing their lids and bottoms, into steam heated cylinders (I) (Fig. 111). Molten hot (80°C) phenol is collected in the heated tank (2) which also acts as a proportioner. Adjacent to it, is a tank (3) for 92% sulphuric acid.

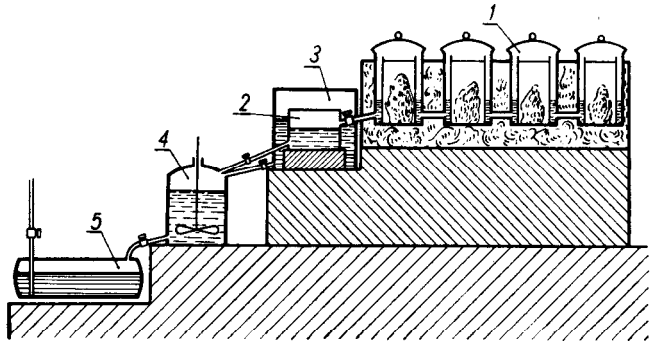


FIG. 111. Diagram of lay-out for sulphonation of phenol (Pascal [2]).

Both liquids flow down to the sulphonator (4), designed for 150-250 kg of phenol. For 100 parts of phenol 500 parts of sulphuric acid is used. The phenol in the sulphonator being hot, the sulphonation reaction starts spontaneously, resulting in a temperature rise to 100°C. After some 10-20 min, sulphonation may be regarded as completed and hot "sulphophenol" is transferred by means of a pressure-egg (5), to the nitrator. The pipeline for conveying the product should be heated, otherwise the phenolsulphonic acids are likely to crystallize.

According to the Lebedev's description [5], phenol is sulphonated with 98% sulphuric acid taken in the proportion of 400-500 parts of acid for 100 parts of phenol. The sulphonation temperature is maintained within 70-80°C or 100-110°C. The reaction time is 4 hr. A temperature of 125-130°C may also be maintained, in which case the reaction time may be reduced to 2 hr. Cast iron sulphonators are used, 2 m in diameter and 1.8 m high. The required temperature may be maintained in the sulphonator by heating with a steel heating coil or with a heating jacket.

A schematic design of a sulphonator used in Great Britain is presented in Fig. 112. The reaction temperature is regulated by adjusting the flow of hot phenol. The propeller stirrer (1) is placed in cylinder (2) to get a better circulation of the reaction mixture. Flat blades (3), mounted above the stirrer, break up the stream of liquid raised by the propeller.

The lid of the sulphonator has an exit for the exhaust pipe, two inlets for introducing the reactants, a manhole, an inlet and outlet for steam passed through the coil and a thermometer hole. In addition to this, the lid is equipped with a sight glass and four handles to open the sulphonator. The heating coil is not shown. This vessel is discharged at the bottom.

If concentrated (98%) sulphuric acid has been used for the sulphonation, the sulphophenol should be diluted with water prior to nitration, otherwise the nitration reaction may proceed too violently. Besides some dilution is advantageous to precipitate any salts present, such as lead or ferric sulphates.

Lebedev [5] advises using wash water from the purification of picric acid, as this effects some economy in nitrating and picric acids.

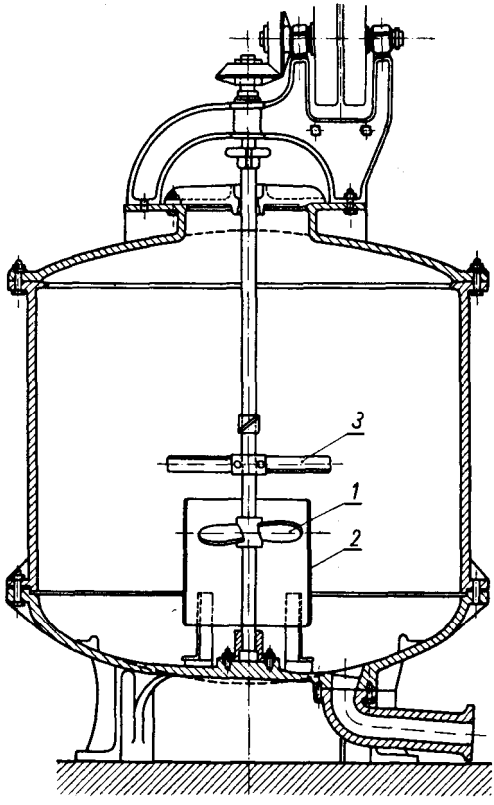


FIG. 112. Sulphonator for phenol (according to Lebedev [5]).

The dilution of sulphophenol is effected in special stoneware vessels. For 95 kg of sulphophenol 72l. of wash water is added. The specific gravity of the sulphophenol after dilution should be 1.35. The diluted sulphophenol is left to settle and then filtered through a sand filter. The temperature of the sulphophenol which is to be nitrated should not be lower than 50°C which is necessary for initiating the nitration reaction.

Nitration of phenolsulphonic acid in movable vessels

The second stage in the manufacture of picric acid is the nitration of the phenolsulphonic acid (sulphophenol) obtained. The simplest reactors used for this process are stoneware jars, "tourills", which may be of various size (e.g. 85 cm diameter

in the widest part, 1.35 m in height). The lids of the jars are equipped with two wide entry holes, 15 cm in diameter (Fig. 113), one for feeding the nitrator with acid and sodium nitrate, the other for connecting the nitrator with the ventilating system. In addition to this, three smaller holes in the lid serve for introducing sulphophenol, inserting a compressed air line that reached down to the bottom of the jar and for inserting a thermometer. Naturally, various modifications of the nitrator construction are possible. These jar-nitrators have the disadvantage of not being equipped with heating or cooling devices: the heat is supplied by the reaction itself and the required temperature is maintained by adjusting the flow of the reactants.

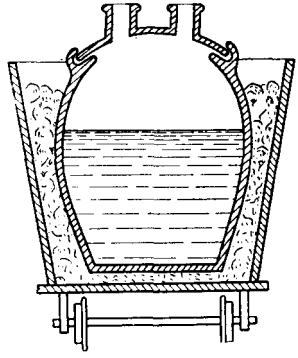


FIG. 113. Jar for the nitration of sulphophenol (Pascal [2]).

To facilitate working and increase output the nitrators are transported in wooden carts from the nitration section to a separate place, where the nitrator contents are allowed to cool prior to their transport to the purification section, where picric acid is separated from the spent acid and washed with water.

Usually the nitrator is tightly enclosed in the cart by a cement layer. This is necessary to isolate and to prevent the nitrator from any damage. Should the jar-nitrator crack because of too high a temperature, the cement layer prevents the reaction mixture from flowing off; sometimes it can even be recovered.

In France nitration was effected in the following way (Pascal [2]).

The jar-nitrator is charged with 275 kg of 44% nitric acid or with the mixture:

nitric acid (44%)	120 kg
sodium nitrate	90 kg

To this 180 kg of warm 50-70°C sulphophenol (corresponding to 30 kg of phenol) is gradually added. At the same time compressed air is passed through the nitrator to mix the reactants well. The rate of addition of sulphophenol should be so adjusted as to prevent the temperature from rising too rapidly at the beginning of the reaction. Hence the sulphophenol should be added carefully at first, although its flow must be rapid enough to attain a temperature of 100°C, at which the main portion of the product nitrates. If the process is operated properly, 95-100°C is attained within 20 min from the beginning of the process (initial temperature 25-30°C).

After one hour a temperature of 115-120°C is attained. All the sulphophenol should be added within one and a quarter hours. By this time the temperature falls to 90-100°C. Then, to remove nitrogen oxides, air is blown through the nitrator for 10-20 min and the nitrator is disconnected from the ventilating pipe and transported to the cooling section.

The nitrator contents are stirred repeatedly with a wooden pole while cooling to prevent picric acid from forming lumps which might retain impurities. After cooling for 34 hr at a temperature of about 60°C, 50-100 1. of water is added, thus preventing the precipitation of sodium bisulphate or, if it has already been precipitated, causing it to go into solution. The diluted acid contains some 45% of H_2SO_4, the concentration at which the solubility of picric acid is lowest. After it has cooled to ambient temperature 12-24 hr, the spent acid is drawn off by a siphon and the picric acid is transported to another section, where it is washed with water. Since the spent acid usually does not contain more than 1% of HNO_3, its recovery is pointless.

As Pascal describes it, a nitrating section is usually designed for 8 nitrators mounted on carts. Every 20 minutes nitration starts (and ends) in a successive nitrator, the whole cycle averaging 2-2.5 hr to complete. Thus during 24 hr, in a battery of 8 nitrators 72 nitrations can be effected. Since each nitrator produces 52 kg per batch, 3744 kg of picric acid will be obtained in 24 hr.

In Russia, as Lebedev reported, the French method gave satisfactory results in summer time only, whereas for the most part of the year (autumn, winter) on account of high heat losses, nitration was never complete and the picric acid yield was low (150-160 parts per 100 parts of phenol). Moreover, the product contained high proportions of mono- and di-nitrophenols.

In this connection various modifications of the process have been developed, consisting first of all in using more nitric acid and less phenol.

The jar-nitrator is charged with 141 kg of 44% nitric acid and 91 kg of $NaNO_3$. Then 172 kg of sulphophenol (which corresponds to 31 kg of phenol) is run into it over a period of nearly 1 hr 40 min. During the last 10-15 min a temperature of 115°C is maintained. Sulphophenol is added in seven equal portions after the following temperatures have been attained:

	Temperature, °C
I	26-30
11	62-70
III	88-89
IV	96-97
V	106-107
VI	111-113
VII	113-115

Since in winter time the cold compressed air used for mixing might cool the reactants, the sulphophenol should be passed into the nitrator in a weaker stream (or the air should be warmed), otherwise it would be difficult to attain the required

temperature. On the other hand, insufficient mixing may cause the formation of undesired lumps of picric acid. Further operations do not differ from those in the process described above.

Nitrogen oxides, as well as nitric acid vapours, generated in the reaction, flow via the ventilating pipe to a system of jars, coolers and absorption towers, where they are absorbed.

There are also other methods in which the procedure consists in first introducing "sulphophenol" to the nitrator and adding the nitric acid afterwards.

Washing picric acid

The contents of 4-5 nitrators (200-300 kg of picric acid) are transferred by means of wooden ladles to a wooden washing vat (Fig. 114), where picric acid is washed several (mostly five) times with 150-200 1. portions of water. For 100 kg of picric acid 400 1. of water is used. The product is tested for purity by determining the SO_4^{2+} ions in a solution of the picric acid in distilled water. After washing, picric acid is separated from water in a centrifuge usually made of copper, the water content being brought to 5-7%.

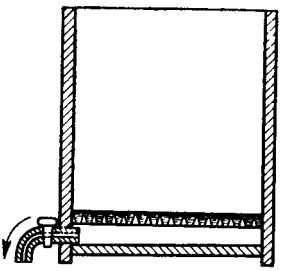


FIG. 114. Wooden vat for washing picric acid (Lebedev [5]).

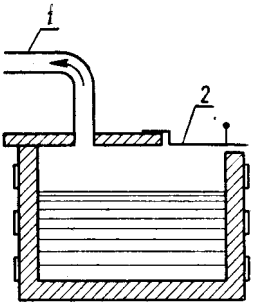


FIG. 115. Nitration tank for the nitration of sulphophenol to picric acid (Pascal [2]).

Washings are collected in special wooden tanks for settling. The spent acid is also added to the washings so as to bring the H_2SO_4 content to 10-30% as in such an "acid water" the solubility of picric acid is at its lowest. The water is decanted from time to time and disposed off into the river, after being neutralized, while the settled picric acid is collected from the bottom of the tank.

The recovered picric acid usually contains large quantities of mineral matter (determined as ash - 0.2%, compared with the permissible limit of 0.03%, as well as H_2SO_4 (0.1% instead of 0.02%). Such a product cannot be used for military purposes without further purification by crystallization from water.

Nitration of phenolsulphonic acid in stationary reactors

The stationary nitrators used in France have the dimensions 2 x 1.8 x 1.0 m (Fig. 115). They are constructed of acid-resistant bricks, joined by an acid-resistant

cement and are reinforced from outside by tarred sheet iron tightened by hoops. The top of the nitrator is partly covered by a Volvic plate equipped with a pipe connected with the ventilating duct (1). An aluminium plate (2) covers the rest of the nitrator top.

In the nitrator described batches of 100-150 kg of phenol may be nitrated: The whole nitration unit is shown in Fig. 116. Nitrators (1) are connected with proportioning tanks for sulphophenol and nitrating acid. Vapours evolving during the nitration flow to jars (3), (4) and (5), passing on their way through the cooling coil (6). Here nitric and nitrous acids are condensed. Non-condensed nitrogen oxides pass to the absorption tower (7), sprayed with water and supplied with air for oxidation. Here the oxides are converted into nitric acid.

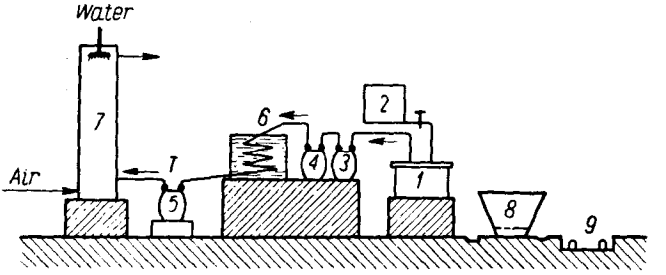


FIG. 116. Flow sheet of the nitration of sulphophenol to picric acid (Pascal [2]).

Next to the nitrator is a wooden double-bottomed tank (8) (the diameter of its upper parts is 1.15 m, height 1.0 m) for separating picric acid from spent acid and for washing the product with water. A narrow gauge railway (9) operates for two lines of nitrators located symmetrically on both its sides.

Similar cylindrical nitrators were in use in Great Britain (Fig. 117).

According to British data, the consumption of raw material for 1 ton of picric acid is:

	British method	French method
Phenol	540 kg	538 kg
$NaNO_3$	1990 kg*	1870 kg
H_2SO_4	2930 kg	2620 kg

* The nitric acid recovered in absorbers from nitrogen dioxide generated in the nitration process, has not been taken into account here. Usually 160 kg of HNO_3 (100%) per 1 ton of picric acid em be recovered.

United States method

During World War I a method of manufacture of picric acid was established in the United States.

Olsen and Goldstein [6] described the method as follows.

302.2 kg of phenol are sulphonated with 605 kg 93% sulphuric atid at 95-98°C during 6 hr. The product is composed of 80% phenol-4-sulphonic acid and 20% phenol-2,4-disulphonic acid.

FIG. 117. General view of nitrators for the production of picric acid [8].

The mixture of phenolsulphonic acids is diluted with 737.5 1. of water. Usually wash-waters are used for this purpose. The concentration of phenolsulphonic acid in the resulting solution is 18.4% calculated on phenol.

Nitration is carried out in two stages. In the first stage the nitrator is filled with a nitrating mixture composed of 70% HNO_3, 10% H_2SO_4 and 20% H_2O. The quantity of the mixture corresponds to that calculated for the introduction of one nitro group. Phenolsulphonic acid is added to the nitrating mixture at 30°C at the beginning and at 52°C at the end. During the first stage mononitro derivatives are formed.

After the first stage the temperature in the nitrator is raised to 60°C and the second stage begins. It consists in adding the same nitrating mixture. During the first hour of mixing the temperature increases to 110-115°C. Altogether 1250 kg of nitrating mixture are added (i.e. 2.75 kg of HNO_3 for 1 kg of phenol).

This method is not accompanied by the evolution of large quantity of nitrogen oxides. The nitration is ended when the content of the nitrator changes colour from red (the colour of phenolsulphonic acids) to yellow (the colour of picric acid).

The yield is 667.6 kg of picric acid, i. e. 220% by weight (theoretical yield 243%).

The spent acid contains 1.0% and 1.5% of picric and oxalic acid respectively. It is diluted with double its weight of water; water from washing picric acid is being

used. The solution is brought to boiling for 5 hr to transform the remaining nitrophenolsulphonic acids into picric acid. After cooling, a second crop of picric acid is obtained in quantity 15% by weight of phenol, i.e. the total yield is 235% by weight. The losses of picric acid in the wash waters correspond to 1% of phenol.

Also Reed [7] described a method of nitrating phenolsulphonic acids in a large pot nitrator of 5500 1. capacity made of acid-proof bricks. Picric acid was settled in a wooden, lead-lined slurry tank and eventually separated in a centrifuge.

CONTINUOUS NITRATION OF PHENOLSULPHONIC ACID

During World War I Brookes [8] introduced in England a continuous method of phenol nitration based on the following principle.

The nitration is performed in a long tank, built of acid resistant bricks joined by a mixture of asbestos and sodium silicate (Fig. 118). The tank is 25 m long,

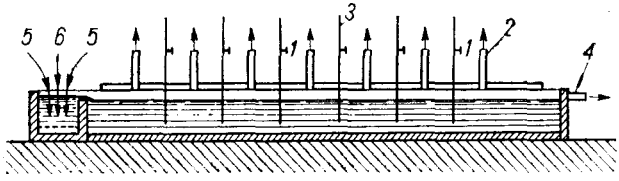


FIG. 118. Diagram of continuous production of picric acid (Pascal [2]).

0.6 m wide, 0.5 m deep inside and with walls 0.2 m thick. At one end of the tank, an area two meters long is separated from the rest of the tank by an inside wall, lower than the walls of the tank. This is a chamber for mixing the reactants. The main part of the tank, 22 m long, is fitted with stoneware covers, equipped with a number of steam pipes (1) for heating up the nitrator content and pipes (2) for conducting away volatile products evolving during the nitration. The reaction mixture flows out continuously through outlet (4) at the other end of the nitrator. A general view of the installation is shown in Fig. 119.

The continuous nitration runs as follows. Phenolsulphonic acid, prepared by reacting 2 moles of H_2SO_4 with 1 mole of phenol, is diluted with water to a sp. gr. of 1.36 and introduced into the mixing chamber by pipe (5). Into it 65% nitric acid and the spent acid from nitration containing about 60% of H_2SO_4 and traces (up to 1%) of HNO_3 are introduced by a set (some 20) of aluminium pipes (6). The total amount of H_2SO_4 introduced is 6 moles per 1 mole of phenol, out of which only 2 moles come from fresh acid. The outlets of all the pipes are arranged below the surface of the liquid. Then the temperature is raised to 102°C by passing steam through the pipes (1). Additional heat may also be supplied by a steam coil, located in this space.

Some picric acid precipitates at the end of the tank and is carried away with the spent acid through the overflow. To facilitate the outflow of picric acid crystals, the reaction mixture coming up to the outlet is agitated now and then by a wooden pole.

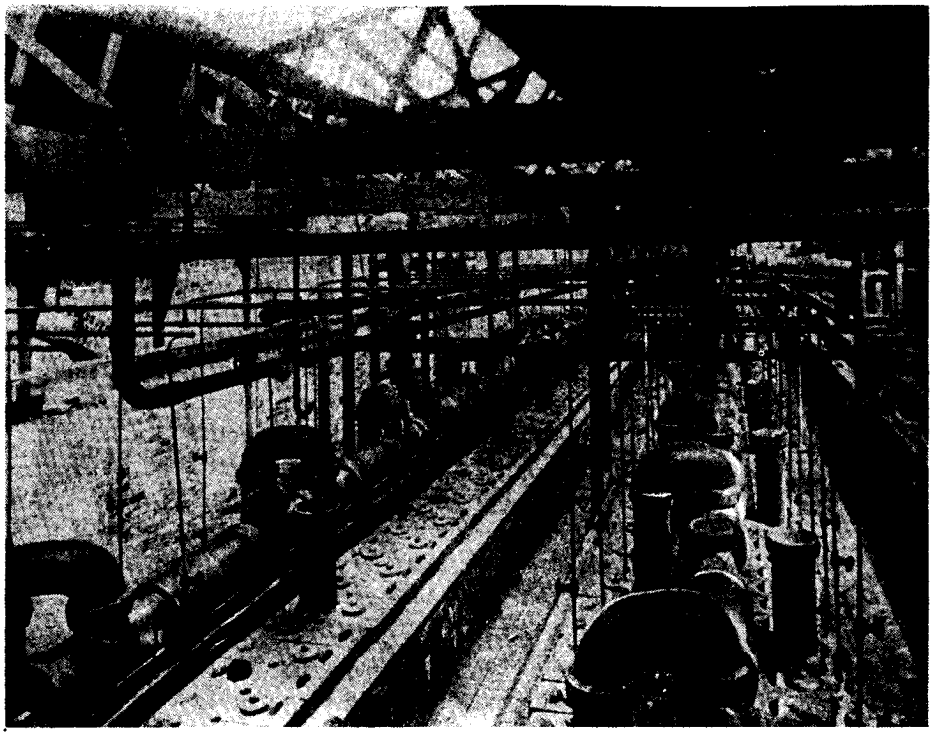


FIG. 119. General view of continuous production of picric acid [8].

The liquid, together with the crystals, is run into a crystallizer equipped with a lead cooling coil and a stirrer rotating at a low speed. Here the rest of the picric acid is precipitated and then separated from the spent acid on a vacuum filter.

Generally the use of lead as a material for construction of a picric acid plant is avoided, except in Great Britain and in the U.S.A. where it is used for the parts of installation which are also in contact with inorganic acids. The latter, being strong acids, are assumed to inhibit the formation of lead picrate.

The spent acid, containing 40-55% of H_2SO_4, is heated to 120°C in an acid-resistant brick tank equipped with an internal lead heating coil. Here the completion of the nitration (conversion of nitrosulphonic acids to picric acid) takes place along with the concentration of the acid. The acid is subsequently transferred to a cooler: crystallizer, similar to that described above, and from there to a vacuum filter for separating picric acid. The spent acid, now containing 60% of H_2SO_4, is returned to the nitration.

By the continuous process 190 parts of picric acid are obtained from 100 parts of phenol. The consumption of acids for the output of 1 ton of picric acid is:

HNO_3 (100%)	1270 kg
H_2SO_4 (100%)	2000 kg

NITRATION WITH CONCENTRATED ACID

The low yield of the nitration with the dilute nitric acid is the principal disadvantage of the above methods. Attempts have been made to use more concentrated acids both for sulphonation and nitration, to increase yield. It has been shown, however, that primitive stoneware installations for nitration, without provision for rapid heating or cooling, or for vigorous stirring, are not suitable for concentrated acids. The classical nitration plant, in which the nitrator is equipped with a heating or cooling jacket as well as with a mechanical stirrer, has proved necessary. Nowadays this is the method of nitration generally used.

Nitration with concentrated acid by the Griesheim method is effected in the following way.

To 400 parts of 30% oleum 94 parts (1 mole) of phenol is added with stirring, the temperature being maintained below 90°C. The mixture is heated to 90-100°C during a period of 5 hr. As a result phenoldisulphonic acid is formed.

The oleum solution is then diluted with 200 parts of sulphuric acid (sp. gr. 1.84). The whole is cooled down to 50°C and 80 parts of 80% nitric acid is added. After the temperature has gone up to 60-80°C, a new portion of 80 parts of nitric acid is added. Finally, when the temperature has exceeded 80°C a further 100 parts of nitric acid is added. Altogether, for 94 parts of phenol 260 parts of 80% nitric acid is used, the excess being 16% over the theoretical amount.

The phenoldisulphonic acid thus prepared is then nitrated in conventional iron nitrators with a jacket and a stirrer. 1000-2000 kg of sulphophenol may be nitrated at a time. From 100 parts of phenol 205 parts of picric acid can be obtained.

A flow diagram of picric acid manufacture by a method applied in the U.S.S.R is presented in Fig. 120 (after Lebedev [5]).

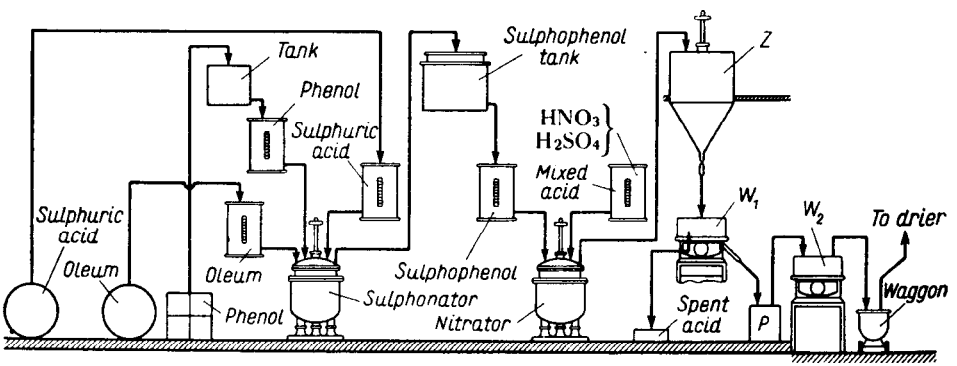


FIG. 120. Flow sheet of the nitration of phenol with concentrated nitrating mixture (Lebedev [5]).

Sulphonation

The first step of the process - sulphonation of phenol - is effected in an iron sulphonator, equipped with a jacket, a heating coil and a stirrer. The construction of the sulphonator is in principle similar to that applied in Great Britain, as described above (Fig. 112, p. 506).

Molten phenol having a temperature of 80°C is transferred to a heated proportioner and from there to the sulphonator, where a quantity of 1750 kg phenol may be sulphonated at a time, this quantity being sufficient for 3-5 nitrations.

After the phenol has been introduced 7800 kg of 20% oleum is fed into the sulphonator. During this operation cold water is passed through the jacket and the coil, the cooling and the flow of oleum being so regulated as to allow the temperature to attain 90°C towards the end of the introduction. Then the cooling is stopped, while the sulphonator content is heated by steam to 100°C and kept at this temperature for 3 hr, before being cooled down again. Then the product is diluted with 3725 kg of sulphuric acid (sp. gr. 1.84). Spent acid may also be used for dilution. This operation should be carried out directly in the nitrator to utilize nitric acid and nitrogen oxides present in the spent acid.

The diluted sulphophenol is cooled down to 35°C before being transferred by compressed air to a sulphophenol tank, heated by a heating coil. The pipe line through which it passes should also be heated up.

The sulphonation takes about 7.5 hr, namely:

Charging with phenol	15 min
Feeding with oleum	21hr
Steam heating	9min
Main reaction	3hr
Cooling	36 min
Dilution	1 hr
Conveying to the tank	36 min
Total	7hr 36 min

The second stage of picric acid manufacture - sulphophenol nitration - is carried out with a mixture of the following composition:

HNO_3	70%
H_2SO_4	20%
H_2O	10%

For easy control the nitration process is divided into 3 stages: (1) mononitration, (2) dinitration and (3) trinitration. All are effected in one nitrator. The acid required is therefore added in three portions, their weights being in the ratio of 80: 80: 100.

Sulphophenol is subjected to nitration, diluted either with fresh sulphuric acid or with spent acid. The dilution with spent acid usually takes place in the nitrator itself just before the nitration process begins.

For this purpose a portion of 1906 kg of concentrated sulphophenol is run into the nitrator and cooled down to 35°C, then during cooling and stirring, 938 kg of spent acid of the composition:

H_2SO_4	76%
HNO_3	0.3-1.5%
HNO_2	2.54%
oxalic acid	2-3%

picric acid	1-2%
total acidity (as H_2SO_4)	83-84%
SP. gr.	1.775

is added. Before starting the nitration the diluted sulphophenol should be cooled down to 40°C.

The separate nitration stages are effected as follows.

Mononitration

To the nitrator containing diluted sulphophenol the first portion of 377.5 kg of the nitrating mixture is run in. During this operation the temperature rises from 40° to 60°C. The addition of the nitrating mixture usually takes 45-60 min (the temperature rises at a mean rate of about 2° per 5 min). At the beginning of the process especially vigorous cooling should be applied to the nitrator contents. Then, as the process goes on, the cooling may be less intense.

Dinitration

In the second nitration stage, another portion of 377.5 kg of the nitrating atid is added. The initial temperature of 60°C rises to 80°C towards the end of the process. The addition of acid takes 45 min. At this stage the nitration proceeds most smoothly and the temperature rises slowly, no cooling being required. If the temperature rises too slowly (less than 2° per 5 min), steam may be passed through the heating coil for a while (not longer than for 1 min) to attain the required temperature by the end of the nitration. If nitration is carried out properly at this stage of the process, it helps the third stage nitration run smoothly. Frothing, which may occur there, may be due to incomplete nitration at the second stage.

Trinitration

At this stage a portion of 470 kg of the nitrating acid is run into the nitrator. The initial temperature is 80°C and towards the end it is 100°C. All the nitrating acid should be added within a period of one hour. The nitrator contents are then kept at 100-110°C for one hour longer. During the addition of the acid the nitrator contents should be cooled. If a rapid rise in temperature occurs the acid flow should be stopped for l-2 min. After all the acid has been added, the nitrator contents should be heated to prevent the temperature falling below 100°C. On the other hand care should be taken to prevent it rising above 112°C. Higher temperatures should be considered dangerous, although British operating conditions for a similar method permit 115°C as the upper limit. A temperature higher than 100°C and close to 110°C favours the formation of larger crystals on cooling.

Nitration completed, the nitrator contents are cooled down to 35°C to precipitate picric acid. The mixture is then transferred by means of compressed air (4 atm) to a higher mounted tank Z (Fig. 120) and from there to the centrifuge W_1 for separating picric acid from spent acid. For each tank a separate centrifuge is provided.

The sulphophenol nitration takes ca. 64 hr, including:

Charging the nitrator with sulphophenol	30 min
Mononitration	1 hr
Dinitration	45 min
Trinitration	1 hr
Heating	1 hr
Cooling	1 hr 20 min
Discharging	30 min
Total	6 hr 15 min

Separation and washing picric acid

Picric acid is separated from spent acid by centrifuging. The centrifuge W_1 shown in Fig. 120 is made of V4A stainless steel. It can work at both low and high speeds. As the picric acid suspension in spent acid is drawn off from tank Z_1 the centrifuge is rotated at a low speed (some 200 r. p. m.), then at full speed. Since the crystals of picric acid may be quite minute the centrifuge basket should be lined with stainless steel gauze.

Picric acid is washed with a small quantity of cold water when still in the centrifuge. Thissash water is then added to the spent acid. The product is discharged at the bottom and transferred to a wooden or aluminium washing tank P, equipped with a mechanical stirrer or with a bubbler. Here, after mixing with water, the stirrer is stopped and, after settling the water, is drawn off by a siphon. After 5-6 washings, the remaining water is removed in centrifuges, W_2, made of tinned copper.

The average charge of the washing tank consists of 350 kg picric acid (the quantity produced in one batch) and 1000 1. of water. The washing operation, comprising charging, mixing, decanting, etc., takes 40-46 min. If the product has formed lumps, it should be crushed in a roll crusher before washing.

Counter-current washing processes also are applied. In a system described by Lebedev [5], acid washings containing some 0.007% of H_2SO_4 coming from centrifuge W_2 which is fed with fresh water, are mixed with acid washings from the picric acid washing tank P containing 1.1% of H_2SO_4. In this way acid water containing 0.85% of H_2SO_4 is obtained. This water is used for washing picric acid in centrifuge W_1. The water flowing out of it contains 3.2% of H_2SO_4. A part of this water is introduced into the washing tank P together with fresh water, in such a quantity as to achieve a content of H_2SO_4 in the washings from the tank P equal to 1.1%, as mentioned above.

Centrifuge W_2 is fed initially with the acid water from washer P, finally with fresh water.

Such a system requires 3 m^3 of fresh water per 1000 kg of picric acid, whereas conventional methods require 10 m^3 of water for the same quantity of picric acid.

After washing, picric acid is centrifuged in centrifuge W_2 so as to reduce its moisture content to 5-6%.

The spent acid flowing out of the centrifuge has a composition as given on p. 515. Its specific gravity 1.775, is similar to that of picric acid (1.813). This is

why the picric acid which has passed through the centrifuge gauze and has precipitated on cooling, does not settle at the bottom but mostly remains suspended in the spent acid. The latter may subsequently be used for dilution of sulphophenol (p. 515).

The spent acid may also be utilized in a different way, namely by diluting with water to a total acidity of 72-75%, further precipitation of picric acid from the solution may be brought about. After a few days standing, the picric acid is separated from the solution on a vacuum filter, as grade II product. The spent acid thus diluted, after being fortified by adding nitric acid and oleum, may be used for the nitration again.

Drying and screening

The construction of picric acid driers presents certain difficulties because of the ready formation of picrates. Having this in mind, wood is mostly used as the construction material for driers, and any metal parts (screws, nails) should be made either of metals that form picrates with difficulty such as copper or aluminium, or of tinned metals or stainless steel. Floors should be made of wood covered with linoleum or concrete coated with asphalt. At the beginning of World War I when concrete floors were commonly in use, picric acid would with time form picrates with cationic constituents of the concrete: calcium, magnesium, sodium and iron. Washing the floor created conditions favourable for the penetration of picric acid into the concrete, and after several months a thick layer of picrates used to form. Any friction, as for example, by moving a bench around or any sort of blow, initiated an explosion of picrates all over the floor, causing fire or explosion in the drier. The inside walls should be plastered with plaster of Paris, since gypsum, being the salt of a strong acid, yields calcium picrate only with difficulty. Lining the walls of the drier section with white glazed wall-paper is recommended. Heaters for heating the drying air should not be placed inside the drying premisses. Workman who have to enter the drying section should put on protective wooden-soled shoes with no nails in them. The floor should be swept frequently and washed with water.

To dry picric acid various drying systems are applied. The chamber drier is the simplest. The design of such a drier, used in the U.S.S.R. is shown in Fig. 121 (after Lebedev [5]). On shelves (I) wooden frames covered with linen are placed. Over each of them about 9 kg of picric acid (calculated on dry mass) is spread, so as to obtain a 3-4 cm thick layer. The heater (2) is located in the passage adjacent to the chamber. The natural flow of the heated drying air is shown in the diagram.

The drying of picric acid with a 7% moisture content at 50-60°C usually takes about 2 days. This period can be cut down to 16 hr by passing the drying air through the heater by means of a ventilator.

Tunnel driers may also be applied for drying picric acid.

For this, mechanical sieves made of aluminium or copper gauze, 50 meshes per 1 cm^2, are used. Figure 122 shows a system which may be used. A wooden funnel (1) serves for leading the product. Lumps of picric acid are retained by gauze (2) and

may be removed from time to time through door (3). Crystals of the required size pass through the gauze into hopper (4).

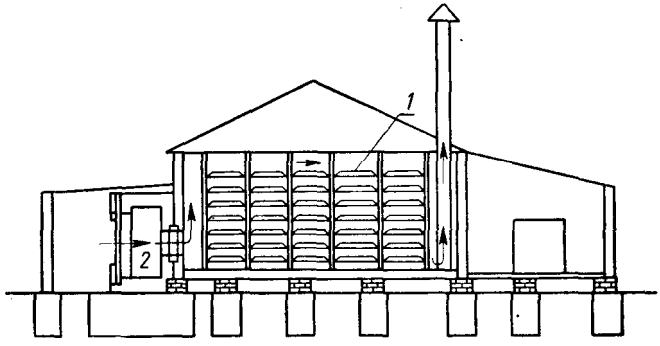


FIG. 121. Chamber drier for picric acid (Lebedev [5]).

The sieve is hung on straps from the ceiling and is kept in oscillating motion by means of an eccentric driven from a compartment adjacent to that in which the screening installation is located. The end product is transported in leakproof chests or in paper-lined barrels.

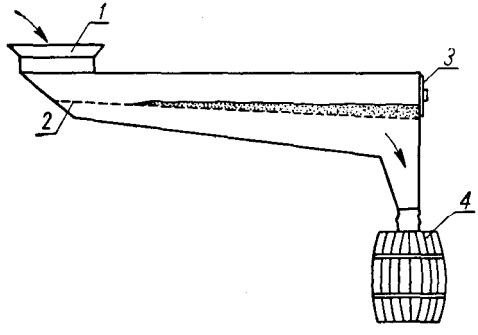


FIG. 122. Sieve for picric acid (Pascal [2]).

DINITROPHENOL NITRATION METHODS

The nitration of dinitrophenol is the most modern commercial method for the production of picric acid from chlorobenzene via chlorodinitrobenzene (for preparation of dinitrophenol from chlorodinitrobenzene, see p. 484).

Both dry and moist dinitrophenol may be nitrated, though the dry product is usually used.

Lebedev [5] describes the production process used in the U.S.S.R. Dinitrophenol from the centrifuge, containing 10-15% of moisture, is dried to obtain a product with only about 0.5% of moisture (drying is effected in picric acid driers).

Since the purity of picric acid depends to a high degree on the purity of the dinitrophenol, the quality standards for the latter should be strictly observed (see p. 486).

The reaction is carried out in a cast iron jacketed nitrator equipped with a stirrer and a stainless steel heating coil 2092 kg of spent acid are run into the nitrator and heated to 50°C. 750 kg of dinitrophenol are then added, the above temperature being maintained during this operation, which will take 30 min. The nitrating mixture prepared from 86% nitric acid (100 parts) and 20% oleum (200 parts) is then run into the nitrator during the course of 23 hr, the excess of the mixture being 25% of HNO_3. During this procedure the temperature should not be allowed to rise over 80°C. After 20 min of stirring, the nitrator contents are heated to 110 - 112°C (1 hr) and subsequently maintained at this temperature for one hour and a half. Altogether the process requires about 8 hr.

The reaction mixture is cooled to 25-30°C as quickly as possible, which takes about 2-3 hr. Picric acid precipitates in fine crystals. The nitrator contents are then drawn off into stainless steel centrifuges or onto iron vacuum filters. The charge of a centrifuge amounts to 250 kg. As a result, 750-780 kg of picric acid can be obtained, which constitutes about 85% of the theoretical yield.

Washing, drying, etc. of picric acid are effected as described above.

A flow sheet of the preparation of picric acid from chlorobenzene is presented in Fig. 123 (after Lebedev [5]).

According to the same author, the material consumption for preparing 1000 kg of picric acid is:

Benzene as feed stock:

Oleum (20%)	2600 kg
Nitric acid (86%)	1320 ,,
Benzene	610 ,,
Sodium carbonate	31 ,,
Chlorine	540 ,,
Sodium hydroxide 85%	680 ,,
Oleum for drying chlorine	95 ,,

Dinitrophenol as feed stock:

Dinitrophenol	1000 kg
Oleum (20%)	950 ,,
Nitric acid (86%)	475 ,,
Spent acid	2370 ,,

METHODS OF NITRATING BENZENE IN THE PRESENCE OF MERCURIC SALTS

During the 1914-1918 War attempts were made to apply industrially Wolffenstein and Böters's method [9] of nitration of benzene in the presence of mercuric salts (p. 110). Vignon [10] developed a method in which a mixture of di- and trinitrophenols in the ratio of about 40: 60 was obtained in nearly 85% yield. A mixture prepared in this way might have been applied directly for filling shells. Nevertheless, the method has not been used on an industrial scale due to the large quantities of mercury required for the production, amounting to about 10% of the benzene

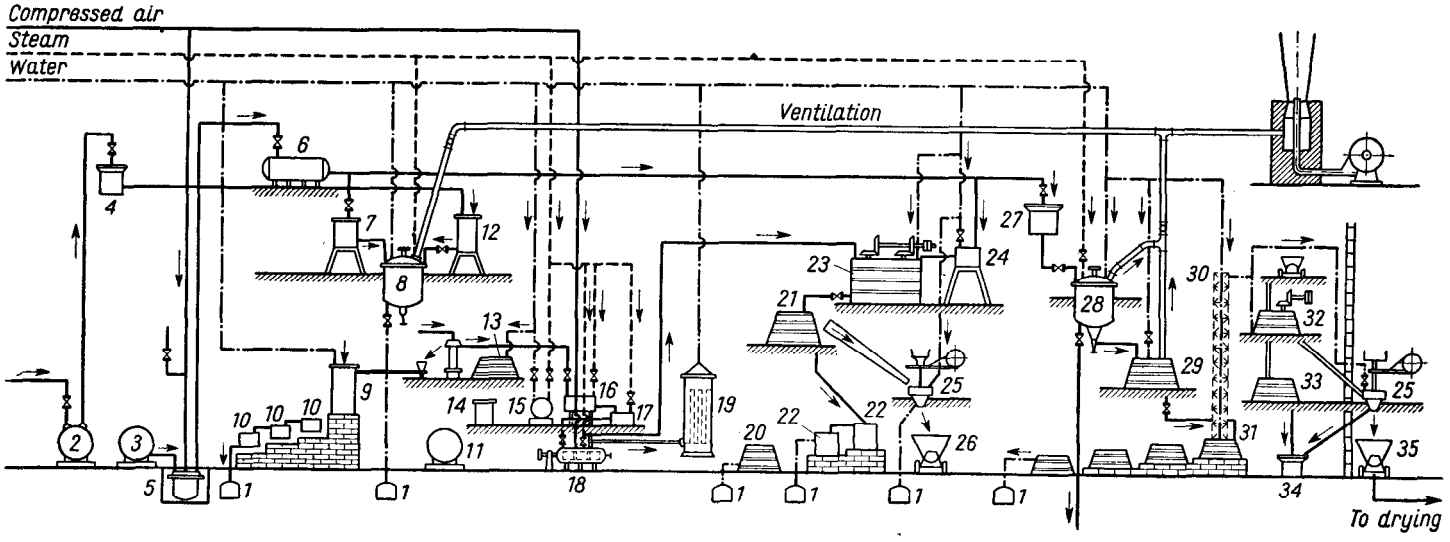


FIG. 123. Flow sheet of the production of picric acid from chlorobenzene (Lebedev [5]).

1 - drain; 2 - storage tank for chlorobenzene; 3 - storage tank for sulphuric acid; 4 - intermediate tank for chlorobenzene; 5 - pressure-egg; 6 - intermediate tank for sulphuric acid; 7 - metering tank for sulphuric acid; 8 - nitrator; 9 - diluting tank; 10 - labyrinth for sedimentation of chlorodinitrobenzene; *11* - tank for caustic soda; 12 - metering tank for chlorobenzene; 13 - vat for washing chlorodinitrobenzene; 14 - metering tank for caustic soda; 25 - tank for hot water; *16* - tank for chlorodinitrobenzene; *17* - metering tank for chlorodinitrobenzene; 18 - reactors for hydrolysis of chlorodinitrobenzene; 19 - condenser; 20 - filter for dinitrophenol from the labyrinth; 21 - filter for dinitrophenol; 22 - labyrinth for the sedimentation of dinitrophenol; 23 - neutralizer; 24 - diluting tank; 25 - centrifuge; 26 - truck with dinitrophenol; 27 - metering tank for sulphuric acid; 28 - nitrator; 29 - filter; 30 - lift; 31 - acid drains; 32 - decantation vat; 33 - titer; 34 - wash-water collector; 35 - truck with picric acid.

used. The recovery of mercury proved to be not worth-while, since its concentration in spent acid and in washing was much too low.

Vignon came to the conclusion that a certain temperature limit should not be exceeded, otherwise oxidation reactions would prevail. In addition, he found that although an excess of benzene resulted in an increased yield, at the same time it favoured the formation of dinitrophenol.

Nitration by Vignon's method on a semi-commercial scale, is carried out as follows: 2.5 parts of mercuric nitrate is dissolved in 100 parts of 52% nitric acid and the solution is mixed with 50 parts of benzene. The mixture is brought to 75-80°C and kept at this temperature for 5-7 hr, then cooled and the layer of benzene, containing nitrobenzene and nitrophenols, is separated by decantation. Benzene is distilled off and nitrobenzene is expelled by steam distillation. The remainder, constituting 125 parts, contains:

dinitrophenol	52%
picric acid	48%

Other authors report the yield obtained does not exceed 140 parts of benzene and the product is contaminated with mercuric picrate.

Broders [11] tried to develop another method of commercial production by passing benzene vapours through nitric acid containing mercuric nitrate. However, he did not succeed in obtaining a yield higher than 20% calculated on the benzene used.

During World War II Wright and his co-workers [12] continued the investigations on this method on large laboratory scale, and developed a process using 1250 ml of benzene for one run.

The reaction was effected at 65°C with 50% nitric acid, containing a dissolved catalyst consisting of

0.28 gramme-atom Al
0.015 gramme-atom Mn
0.0005 gramme-atom Al

calculated on 100 g of benzene. The yield obtained was 150 g of picric acid from 100 g of benzene, i.e. 50% of the theoretical. The consumption of nitric acid amounted to 140-160 g (calculated on HNO_3). Nitrobenzene and dinitrobenzene were formed as by-products.

Wright suggested the recovery of the nitrogen dioxide generated in the reaction and the recycling of spent acid to utilize the catalyst it contains. The results obtained by the author do not differ in principle from those of the earlier investigations. The method, however, like the earlier ones, has not found industrial application.

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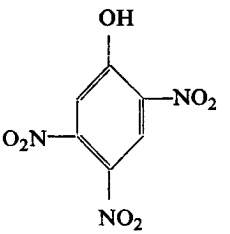
CHAPTER XV

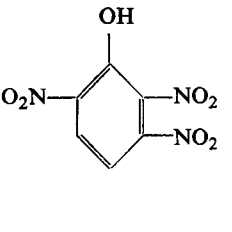
OTHER NITRO DERIVATIVES OF PHENOLS

PICRIC ACID ISOMERS

APART from picric acid, unsymmetrical β– and γ– trinitrophenols are known:



β

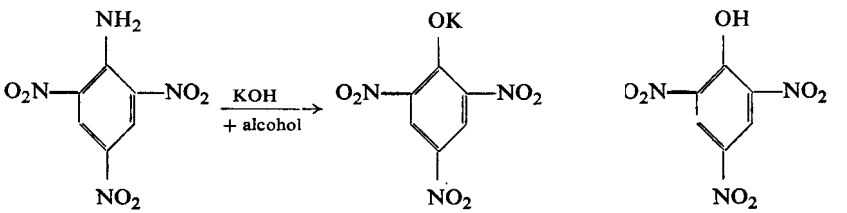


γ

The β– isomer or 2,4,5-trinitrophenol (m. p. 96°C) may be obtained by nitration of 3,4-dinitrophenol, the γ– isomer or 2,3,6-trinitrophenol (m. p. 118°C) by nitration of 2,3-dinitrophenol. Since they are not formed during the nitration of phenol, they are not present in picric acid and are not of any practical importance.

"ISOPICRIC ACID"

Nietzki and Dietschy [1] found the product they obtained by reacting an alcoholic solution of KOH with "trinitro-phenylhydroxylamine" (which later was proved to be trinitroaniline, as Borsche [2] showed in his investigation already mentioned) was a potassium salt of "isopicric acid" :

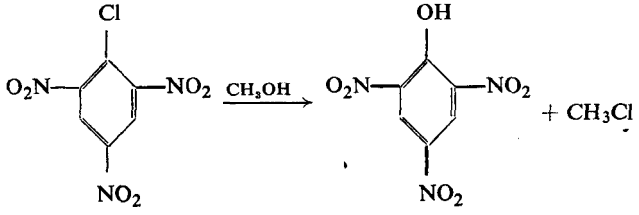


(1)

The melting point of the latter is close to that of picric acid (117-118°C) but

the properties of its potassium salt (as for example the solubility) differ from those of potassium picrate.

The investigations of the above authors were checked by Desvergnes [3], who found the melting point of "isopicric acid" to be 119.7°C. Moreover, he was able to observe that picryl chloride, on boiling in water, alcohol or pyridine also gives a certain quantity of "isopicric acid", according to the equation:



(2)

The evidence for the existence of "isopicric acid" is not convincing.

PICRIC ACID SALTS

Metal salts of picric acid may be formed by the action of picric acid on metals, their oxides or carbonates and in certain cases also on their other salts. They are crystalline substances, mostly more sensitive to friction, impact and heat, than picric acid itself. Due to their high sensitivity to stimuli, the explosive properties of picrates were known long before those of picric acid.

Picrates formed by precipitation from aqueous solutions contain water of crystallization which may desensitize them. For example, the decahydrate of ferric picrate shows no sensitiveness to friction and impact and cannot be ignited when in direct contact with a flame, whereas the anhydrous compound is exceptionally sensitive to these stimuli.

The properties of picrates have been examined by several authors, e.g. Cheltsov [4], Will [5], Silberrad and Phillips [6], Kast [7], Krauz and Turek [8], Tucholski [9] and T. Urbanski and Slon [10].

Tucholski determined the dehydration temperatures of picric acid salts hydrates, their melting points, initiation temperatures and temperatures preceding explosion. T. Urbanski and Slon determined their sensitiveness to impact and flame.

The results obtained by the above authors are presented in Table 119.

All picrates, especially lead, barium, calcium, iron and nickel picrates, should be considered as highly undesirable in picric acid. They have caused a great number of accidents. Among them only potassium picrate has found some practical uses, viz. in some high explosive and propellant compositions no longer in use at the present time.

Nowadays the only picrates applied as explosives for military purposes are ammonium and lead picrates, the latter being an initiating explosive (Vol. III).

TABLE 119

PROPERTIES OF PICRIC ACID SALTS AND THEIR HYDRATES

According to Tucholski [9]					According to T. Urbanski and Slon [10]		
Picrate	Content of water of crystallization	Temperature of dehydration to the next lower hydrate °C	Melting point °C	Initiation temperature °C	Sensitiveness to impact (10% explosion) 2 kg	Sensitiveness to impact (10% explosion) 10 kg	Sensitiveness to flame (number of swings*)
Na	1 H_2O	154					
	anhydrous	-	210	313		19 cm	18
Mg	9 H_2O	59					
	6 H_2O	82					
	4 H_2O	125					
	2 H_2O	208					
	anhydrous	-	-	368		no explosion	9
Al	16 H_2O	58					
	13 H_2O						
	3 H_2O	156					
	anhydrous		-	390-395			71
K	anhydrous	-	250	331	21 cm	10 explosion	10.5
Ca	8 H_2O	14					
	6 H_2O	91					
	5 H_2O	122					
	1 H_2O	228.5			8 cm		10
	anhydrous	-	316	323			
Cr	2 H_2O	14					
	anhydrous	-	275.5	296.5	28 cm		53.5
Mn	8 H_2O	68.5					
	3 H_2O	130					
	anhydrous	-	-	289		60 cm	14.5
Fe II	8 H_2O	75					
	4 H_2O	97					
	anhydrous	-	275.5	296.5			
Fe III	10 H_2O	72.5					
	1 H_2O	100					
	anhydrous	-	155	247	10 cm		1
Co	8 H_2O	40					
	6 H_2O	78					
	2 H_2O	168					
	anhydrous	-	226	327.5,			
Ni	6 H_2O	35.5					
	5 H_2O	48					
	4 H_2O	94.5					
	1 H_2O	173.5					
	anhydrous	-	40-25~	348		40 cm	5.5

* Nitrocellulose ignites from 1 swing, gunpowder from 8 wings.

TABLE 119 (continued)

Picrate	According to Tucholski [9]				According to T. Urbanski and Slon [10]		
	Content of water of crystallization	Temperature of dehydration to the next lower hydrate	Melting point	Initiation temperature	Sensitiveness to impact (10% explosion)		Sensitiveness to flame (number of swings*)
		°C	°C	°C	2 kg	10 kg	
Cu	11 H_2O	30					
	8 H_2O	35					
	5 H_2O	12					
	3 H_2O	120.5					
	anhydrous	-	-	290	30 cm		16
Zn	10 H_2O	51					
	8 H_2O	54.5					
	6 H_2O	101					
	2 H_2O	151					
	anhydrous	-	-	303		no explosion	35
Sr	5 H_2O	87					
	1 H_2O	216			17 cm		
	anhydrous	-	290	341			
Ag	anhydrous	-	296	332			
Cd	7 H_2O	44					
	4 H_2O	69					
	1 H_2O	144					
	anhydrous	-	-	328			
Ba	6 H_2O	46.5					
	5 H2O	63					
	2 H_2O	86					
	1 H_2O	195			2.5 cm		4
	anhydrous		200	332			
Hg	4 H_2O	65					
	3 H_2O	ca. 103					
	1 H_2O	ca. 144	ca. 290	333			
Tl	anhydrous	-	-	301			
Pb	1 H_2O	130					
	anhydrous				2 cm		10

• Nitrocellulose ignites from 1 swing, gunpowder from 8 swings.

AMMONIUM PICRATE

There are two forms of ammonium picrate: yellow and red. Cahours [11] drew attention to this fact in 1849. Anselmino [12], Stepanov [13] and a number of other authors have studied the problem of the existence of two differently coloured forms of the compound. Dehn and Ball [14] expressed the opinion that the two forms of ammonium picrate are, as Hantzsch suggested, chromoisomers, and that the phenol form should be assigned to the yellow modification, while the red one

should be regarded as the quinonoid form. Hale [15] found that the colour of ammonium picrate was darker (more red), the more concentrated the ammonia used for the neutralization of the picric acid. By heating to 150°C the red form changed into the yellow one.

T. Urbanski, Hackel and Galas [16] found that it was the pH of the solution in which picric acid was neutralized that was responsible for the colour of ammonium picrate crystals. The higher the pH the more readily the red crystals were formed. By neutralizing picric acid with an ammonium carbonate solution the authors always obtained a yellow product, whereas by using a 25% ammonia solution for neutralization, they obtained a red product. Both forms were found to have equal specific gravities, 1.6715, whereas they differed somewhat in their densities of loading when pressed. At low pressures, densities of loading of the red form were slightly higher. At high pressures the yellow form was observed to have the higher density (Table 120).

This difference in density values should be ascribed to the physical properties of crystals. At low pressures the crystals of the red form, due to their shape, can be packed more easily in a given space. At high pressures a lower mechanical strength of the yellow crystals plays a part, viz. being disintegrated they more readily fill up the space.

TABLE 120

DENSITY OF AMMONIUM PICRATE FORMS

Pressure, kg/cm^2	Density, g/cm^3	
	yellow form	red form
0 (loose)	0.891	1.045
110	1.244	1.299.
330	1.396	1.392
660	1.490	1.490
1100	1.553	1.529
1540	1.593	1.562
1910	1.596	1.569
2540	1.616	1.582

The above authors, in a detailed study of the explosive properties of the two forms of ammonium picrate, found no difference in their explosive power. However, the red form is slightly more difficult to bring to explode and it is to this property that differences in the figures obtained in determination of their explosive properties may be ascribed.

Here are the principal data obtained by T. Urbanski, Hackel and Galas [16]:

Sensitiveness to impact: 10% explosions from a 10 kg weight falling from a height of ca. 20 cm, which is in agreement with Kast's results [7]
sensitiveness to flame: yellow ammonium picrate ignites after 8 swings; the red form after 12.5 swings
initiation temperature (20°/min) 257-259°C
specific pressure, f (experimentally) 7200 m
expansion in the lead block test 330-335 cm^3

TABLE 121

DETONATION RATE OF AMMONIUM PICRATE (BOTH FORMS) AT VARIOUS DENSITIES (IN A STEEL PIPE 35/42 mm)

Density, g/cm^3	Detonation rate, m/sec	
	yellow form	red form
0.86	4380	-
1.11	-	5155
1.34	5835	-
1.35		5835
1.49	6950	-
1.50	-	6960
1.55	6995	-
1.56	-.	6995
1.58		6200
1.60	6030	-

As the highest rate of detonation under the above condition, 7000 m/sec for both forms has been taken. Thus, ammonium picrate should be considered as a somewhat more powerful explosive than TNT.

The thermochemical properties of ammonium picrate have been examined by several authors (no indication given as to the colour of the substance examined). Sarrau and Vieille [17] determined its heat of combustion as ranging from 693.2 to 708.9 kcal/mole.

T. Urbanski and Soroka [18] determined heats of combustion of the two forms and from these they calculated their heats of formation:

	Heat of combustion $(-\Delta H_R)$	Heat of formation $(-\Delta H_f)$
yellow form	687.3 kcal/mole	83.7 kcal/mole
red form	677.3 kcal/mole	93.7 kcal/mole

It can be seen that the calculated heat of explosion of the red form is somewhat lower than that of the yellow one.

These results do not agree with Hale's data. He reported the fragmentation of 3 in. shells might indicate the higher explosive power of red ammonium picrate, and the equal abilities of the two forms to detonate under the influence of a detonator.

Ammonium picrate under the name of Explosive D was first used in the United States in 1901. It was Dunn [18a] who proposed using it as a high explosive material for filling shells. During both the World Wars armour piercing shells of the U. S. Navy were filled with this explosive. It is thought that ammonium picrate is less sensitive to impact and friction than TNT, and that is why it was used for the purpose. However, the above mentioned investigations by T. Urbanski and his co-workers did not confirm the view. Moreover, they revealed that ammonium picrate, and especially its yellow form, was easy to ignite when in contact with a flame, its flammability being of the same order as that of gunpowder.

GUANIDINE PICRATE

Guanidine picrate may be obtained by acting with a warm aqueous solution of ammonium picrate on an aqueous solution of guanidine nitrate. A yellow, crystalline precipitate of guanidine picrate (m. p. 319°C, with decomposition) is formed.

Guanidine picrate has been suggested in the United States as a high explosive, being of exceptionally low sensitivity to impact and friction.

DANGER PRODUCED BY PICRATES

If picric acid is free from picrates, its burning, even in large quantities, does not present any risk of explosion. A case is known (in the U.S.A.) when 100 tons of picric acid caught fire. It burned relatively smoothly although the flame attained a height of 10-15 m and a characteristic loud whistling noise was heard. Slight explosions were observed only when roof fragments fell into the burning mass, causing blast from a violent eruption of confined gases. However, had picrates been present, such a fire might have ended with a violent detonation but according to Sapozhnikov [19] it is sufficient for molten picric acid merely to come into contact with metal to create favourable conditions for the formation of picrates.

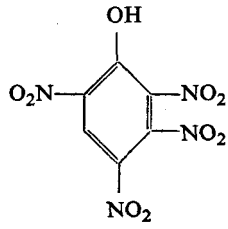
A violent explosion of picric acid in a Manchester factory in 1887 was ascribed to the formation of picrates. Burning, molten picric acid flowed down onto lithopone, forming lead picrate which in consequence caught fire. The latter, being an initiator, detonated and caused the picric acid to detonate.

A fire, followed by an explosion at Huddersfield in 1900 was also caused by detonation of iron picrate (presumably Fe^{2+}). The iron picrate had been formed on the surface of steam pipes located in the picric acid drier shop. It ignited when a plumber, unaware of the fact, struck one of the pipes with a hammer. The flame spread along the pipe and set the drying picric acid on fire.

In a French factory streaks of picric acid had been formed alongside a narrow gauge railway. As the soil beneath was calcareous, calcium picrate formed which, having dried up in the summer, was ignited by friction or a blow, spreading flames all over those parts of the factory marked with calcium picrate streaks.

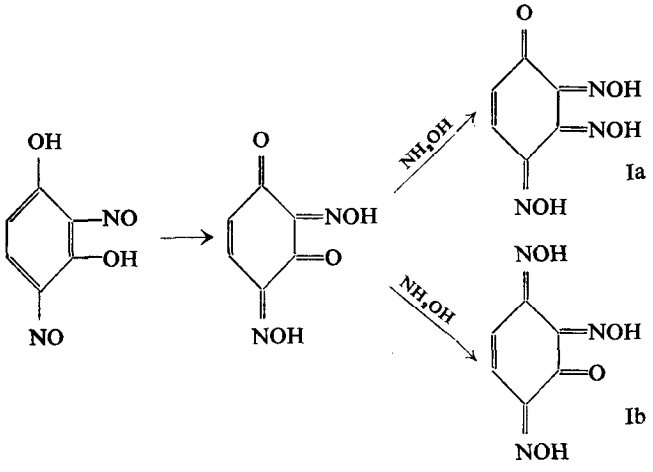
TETRA- AND PENTA-NITRO DERIVATIVES OF PHENOL

TETRANITROPHENOL



This compound (m. p. 140°C) was obtained by Nietzki and Burckhardt [20]

from diquinoyltrioxime. The latter can exist in two isomeric forms, (Ia) and (Ib), which may be prepared by reacting hydroxylamine with dinitrosoresorcinol:



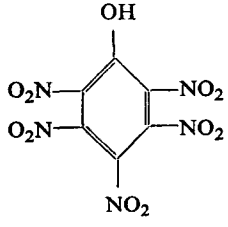
Tetranitrophenol forms by the action of 50% nitric acid followed by a 63% acid on diquinoyltrioxime at a temperature lower than the room temperature. By neutralizing the solution a sparingly soluble potassium salt is precipitated, which in turn may be converted by double decomposition into a still less soluble barium salt. From the latter, by the action of a calculated quantity of sulphuric acid, free tetranitrophenol may be obtained.

A product of higher purity than that obtained by Nietzki was prepared by Blanksma [21] by the nitration of *m*- nitrophenol with a mixture of nitric acid (sp. gr. 1.52) and concentrated sulphuric acid. As shown later (van Duin and van Lennep [22]) the product, if of high purity, exhibits fairly high stability against heating. It explodes at 245-251°C, whereas if it is contaminated it decomposes after it has been brought to its melting point, i.e. to 140°C.

The nitro group in position 3 in tetranitrophenol is very reactive. On boiling with water the compound yields trinitroresorcinol. With methyl alcohol it forms trinitroresorcinol monomethyl ether. With an alcoholic ammonia solution, tetranitrophenol gives aminotrinitrophenol.

Tetranitrophenol is more sensitive to impact than tetryl (van Duin and van Lennep [22]).

PENTANITROPHENOL



Pentanitrophenol (m. p. 190°C) was obtained by Blanksma [21], who nitrated 3,5-dinitrophenol with an anhydrous mixture of nitric and sulphuric acids. The product was precipitated, and could then be recrystallized from chloroform.

Both meta-nitro groups are reactive. With water, pentanitrophenol yields trinitrophloroglucinol, with alcoholic ammonia solutions it gives diaminodinitrophenol.

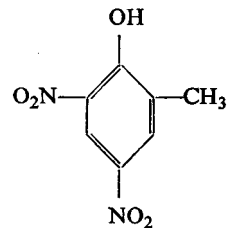
NITRO DERIVATIVES OF CRESOLS

Of the three isomeric cresols: *ortho-*, *meta-*, and *para-*, only *m-* cresol can be used as the starting material for introducing three nitro groups, viz. in the 2,4,6-positions. *Ortho* and *p-* cresols are able to form stable nitro group systems only when no more than two nitro groups are introduced. Under the conditions of the nitration of *m-* cresol to its trinitro derivative the o- and *p-* isomers are oxidized to oxalic acid.

Cresol for nitration should contain a high proportion of the *m-* isomer. Commercial "meta-cresol" usually contains about 60% of the *m-* isomer and 40% of *p-* cresol. The preparation of a much more costly raw material, containing 90% of *m-* cresol is also possible. It is clear that the yield of trinitro-m-cresol will correspond to the *m-* cresol content in the starting product.

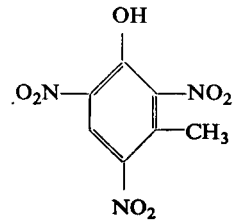
A methyl group present in the ring facilitates the introduction of nitro groups. This is why *m-* cresol is more readily nitrated than phenol. On the other hand a methyl group enhances oxidation processes. This accounts for the lower yield of trinitrocresol obtained, as compared with that of picric acid. Like picric acid, trinitrocresol has the disadvantage of readily forming metallic salts which are sensitive to impact.

All these factors have limited the practical application of trinitrocresol. France was the only country which used it, under the name of "Cresilite" mostly in mixtures with other nitro compounds to lower their melting points (Vol. III). Among nitro derivatives of cresols, dinitro-m-cresol (m. p. 86.5°C)



is of some practical importance, though not as an explosive but as a herbicide.

2,4,6-TRINITRO-m-CRESOL



Physical properties

2,4,6-Trinitro-m-cresol (m. p. 107-107.5°C) is less soluble in water than picric acid. With 100 g of water the following quantities go into solution:

at 6°C	0.15 g
15°C	0.2 g
100°C	1.83 g

Benzene dissolves 2,4,6-trinitro-m-cresol more readily than picric acid:

at 6°C	9.2 g
15°C	13 g

The compound is readily soluble in alcohol, ether and acetone.

Trinitro-m-cresol may be separated from picric acid in the form of its potassium salt, taking advantage of a difference in the solubility of the potassium salts of the two compounds, as shown below:

	Grammes of salt in 100 ml of water		
	at 6°C	at 15°C	at 100°C
potassium picrate	3.3	0.45	14.55
potassium trinitrocresate	1.4	3.4	over 50

On the other hand, trinitrocresolates of organic bases are more difficult to dissolve than the corresponding picrates. Solubilities in 100 ml of water of pyridine picrate and pyridine trinitrocresolate are given below for comparison:

	at 20°C	at 100°C
pyridine picrate	0.36 g	12.6 g
pyridine trinitrocresate	0.12 g	1.5 g

The specific gravity of trinitro-m-cresol is 1.64. Under a 1500 kg/cm^2 pressure this of 1.55 can be obtained, and under 2900 kg/cm^2 - 1.63.

Chemical properties

2,4,6-Trinitro-m-cresol forms addition compounds with aromatic hydrocarbons in the molecular proportion of 1:1:

	melting point, °C	
with naphthalene	124.5	(Sapozhnikov, Rdultovskii [23])
„ acenaphthene	118	(Jefremov [24])
„ phenanthrene	113	„
„ fluorene	107	„
„ retene	118	„

On the whole the properties of trinitro-m-cresol are similar to those of picric acid. The properties of trinitrocresolates differ only slightly from those of picrates, as for example their lead salts. Ammonium trinitrocresolate has been used to some extent in Austria as a high explosive for filling shells.

Thermochemical and explosive properties

When heated, trinitro-m-cresol decomposes at about 200°C and at 275°C explodes. Its sensitiveness to impact is similar to that of picric acid, but its ability

to detonate is lower. Thus, when compressed to a density of 1.63 it requires a powerful detonator (at least 2 g of mercury fulminate). Picric acid of the same density can be detonated by 0.6 g of the same detonator.

The following figures characterizing the explosive properties of trinitro-m-cresol were given by Kast [7]:

heat of explosion	925 kcal/kg
volume of gases, V_0	675 l./kg
temperature of explosion	2700°C
maximum rate of detonation	6850 m/sec
specific pressure, *f*	7595 m
expansion in the lead block	275 cm^3 (i.e. 90% of that given by picric acid)

The heat of the formation ($-\Delta H_f$) of trinitro-m-cresol is +54.1 kcal/mole, according to Koehler [25].

MANUFACTURE OF TRINITRO-m-CRESOL

In industrial practice, trinitro-m-cresol is prepared by the nitration of cresol. The manufacturing process is similar to that used for picric acid. It consists of two stages - sulphonation and nitration. However, due to the liability to oxidation, its yield does not exceed 150-160 parts from 100 parts of pure *m*- cresol, i.e. a maximum of 67-73% of the theoretical yield.

From 100 parts of commercial "meta-cresol" containing only 60% of the *m*- isomer (the rest being *p*- cresol) not more than 100 parts of trinitro-m-cresol can be obtained. *p*- Cresol is fully oxidized to oxalic acid, which then crystallizes from the spent acid.

The isolation of pure *m*- cresol has proved to be too expensive because the boiling points of the *m*- and *p* -isomers are too close to each other:

	boiling point, °C	melting point, °C
m- cresol	201	11-12
p- cresol	202	36
o- cresol	185	31

Experiments have been carried out to separate ***m*-** and *p*- cresols by sulphonation, as sulphonated *m*- cresol is a liquid substance, while sulphonated *p*- cresol is crystalline. The two isomers were then separated by centrifugation. However, the purity of the product obtained was not satisfactory enough, thus the process would not be economical.

In the absence of any other criteria, a sample of each "meta-cresol" batch to be nitrated should be subjected to a laboratory nitration test.

The process of cresol nitration is much the same as that for phenol. In France, where the output of Cresilite was highest, movable stoneware jar-nitrators ("tourills"), or the stationary type described above were used for the nitration (pp. 506, 509).

Nitration of *m*- cresol in stationary nitrators was carried out as follows:

1860 kg of 52% nitric acid is charged into the nitrator, followed at a fairly high rate by sulphocresol (obtained by sulphonation of 200 kg of commercial "meta-cresol" with 600 kg of sulphuric acid, sp. gr. 1.84, as described above in the picric acid

manufacture). After the temperature in the nitrator has attained 45°C (which requires about 45 mm), the flow of sulphocresol is stopped.

The temperature rises spontaneously to 85°C and sulphocreso1 is then run in again at such a rate as to introduce the whole lot in no more than 2 hr. Towards the end of the process the temperature attains 100-103°C. The reaction mixture is allowed to remain at rest for half an hour, then compressed air is gently blown through for about 20 min, thus causing the temperature to fall to 90°C. A further temperature fall to 70°C is achieved by blowing air strongly for about one hour. At this stage of the process the granulation of the Cresilite begins, depending on the cooling rate and on the intensity of the air blowing.

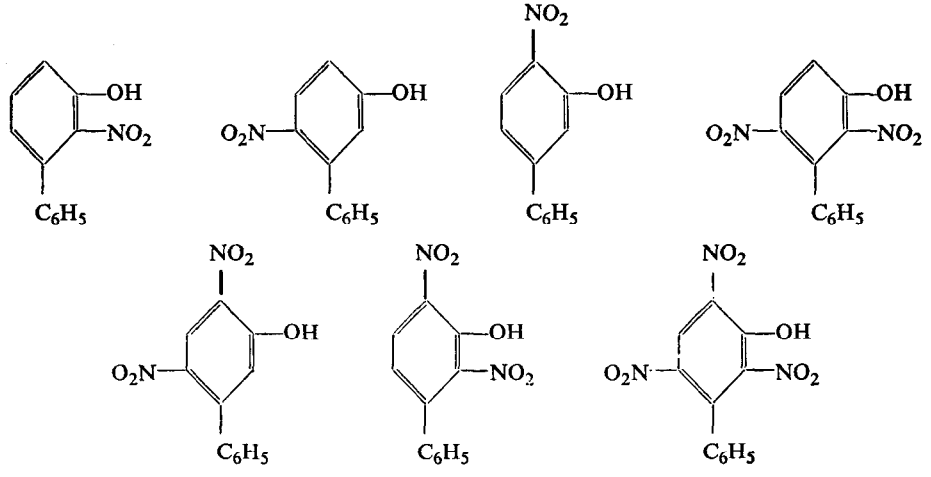
After granulation has been completed, the nitrator contents are allowed to remain at rest for 12-15 hr, then without any dilution the spent acid are drawn off by means of an aluminium siphon. The spent acid is passed through an asbestos filter to retain any Cresilite granules carried away.

The product obtained is in the form of yellowish-brown granules, with a melting point of 101-103°C.

NITRO DERIVATIVES OF ARYLPHENOLS

NITRO DERIVATIVES OF 3-HYDROXYDIPHENYL

Colbert, Fox and Matuszak [26] nitrated 3-hydroxydiphenyl and obtained a number of its nitro derivatives:



NITRO DERIVATIVES OF POLYHYDRIC PHENOLS

Among polyhydric phenols, only the nitro derivatives of resorcinol have gained considerable practical importance. The nitro derivatives of phloroglucinol may also be of some value. Both phenols have hydroxyl groups in the *meta* position to each other, thus enabling the introduction of three nitro groups. Among dinitro derivatives, those of pyrocatechol have found some uses.

The presence of a large number of hydroxyl groups in the ring increases the reactivity of phenol very considerably. That is why these compounds are very easy to nitrate, and in the nitration process by the conventional method for phenols, i.e. via sulphonation, followed by nitration, three nitro groups usually enter the compound. This is also the reason why the preparation of, for example, a nitro derivative of resorcinol with less than three nitro groups, requires the application of special methods. They may be divided into three groups.

1. Nitroso groups are introduced and subsequently they are oxidized to nitro groups. Since for each phenolic group one nitroso group can be introduced, the method may be applied for the preparation of nitro derivatives of polyhydric phenols in which the number of nitro groups is equal to the number of hydroxyl groups (e.g. dinitroresorcinol). The method is also applied when polyhydric phenols nitrate very easily (e.g. phloroglucinol), since their direct nitration proceeds too violently, and by breaking the process into two stages - nitrosation and oxidation of the nitroso groups - it can be made to run more smoothly.

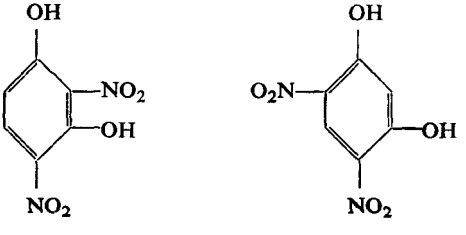
2. A compound is nitrated which in addition to phenolic groups contains some other which inhibits the introduction of nitro groups and after the nitration becomes so mobile that it can readily be removed. A carboxylic group may serve the purpose. For example, by the nitration of resorcylic acid, dinitroresorcinol may be obtained as an end product (for more details see p. 537).

3. Halogenated phenols or polyhalogen derivatives of benzene are nitrated. After the compound has been nitrated, the halogen atom or atoms become reactive and may be removed by hydrolysis. This method, which is widely utilized in the preparation of dinitrophenol, has not found wider practical application because of difficulties in obtaining supplies of the corresponding starting materials (some halogen compound;).

Among all the possible nitro derivatives of resorcinol only di- and tri-nitroresorcinols are of practical value. Both are used as initiating explosives in the form of lead salts (Vol. III). The lead salt (Pb^{2+}) of dinitroresorcinol is also of some practical value and in this connection some data characteristic of the compound will be given.

DINITRORESORCINOL

Two isomers of dinitroresorcinol, 2,4- (or 2,6-) and 4,6-dinitroresorcinols are known (m. p. 148°C and 212.5°C respectively).

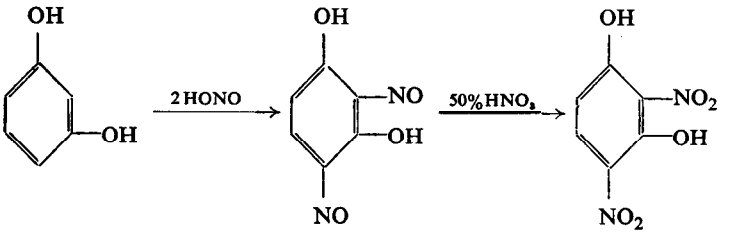


They are yellow substances, readily soluble in hot water, which dye animal fibres and leather.

Only the 2,4-isomer is of practical importance as the one most easily available. The 4,6-isomer cannot be obtained directly, though it may be prepared by the nitration of diacetylresorcinol.

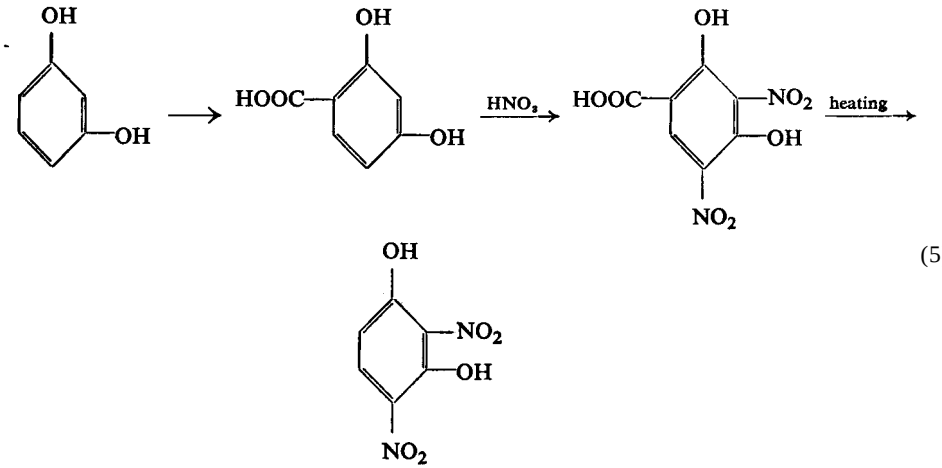
Since the nitration of resorcinol by the conventional method for phenols (i.e. sulphonation followed by the action of nitric acid) yields a trinitro derivative, two other methods for the preparation of dinitroresorcinol are possible, viz.: oxidation of dinitrosorcsorcinol or nitration of resorcylic acid followed by decarboxylation.

According to Kostanecki and Feinstein [27], the following reactions take place in the former process:



(4)

Hemmelmayer [28] presented the nitration of resorcylic acid and its subsequent decarboxylation by the following reactions :



(5)

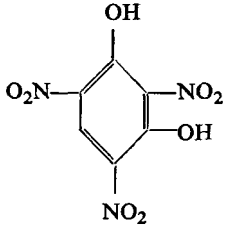
In practice the first process is applied, as it gives a higher yield of the product.

The nitrosation is effected in a well known way. A weak (2.75%) aqueous solution of one mole of resorcinol is acidified with 2 moles of sulphuric acid. The solution is cooled down to -2°C and a 10% aqueous solution of 2 moles of $NaNO_2$ is added, dropwise. Crystalline yellowish 2,4-dinitrosoresorcinol is precipitated in theoretical yield. The precipitate is washed and separated in a centrifuge or on a vacuum filter prior to oxidation. From dinitrosoresorcinol the divalent lead salt of dinitrosoresorcinol may be prepared, having initiating properties.

Dinitrosoresorcinol is oxidized with 50% nitric acid at a temperature below 0°C. Moist, freshly prepared dinitrosoresorcinol is charged into the reactor, containing nitric acid cooled down to -5°C. When calculating the concentration of nitric acid, the water content in dinitrosoresorcinol should be taken into account. Simultaneously with the dinitrosoresorcinol concentrated nitric acid is introduced into the reactor to keep the concentration of the acid in the reactor constant. After the reaction has been completed, the reactor contents are run out into icy water. The volume of the water containing ice should be several times as large as that of the product. Dinitroresorcinol is precipitated and is separated on a vacuum filter and washed with a small quantity of cold (ca. 0°C) water. The crude product contains some trinitroresorcinol. By crystallization from hot water a product is obtained which should not melt below 147°C. The yield of the reaction, calculated on the resorcinol used, is about 30% of the theoretical.

For the preparation of the divalent lead salt a moist product is used; its water content should be determined exactly.

TRINITRORESORCINOL (STYPHNIC ACID)



Physical properties

Trinitroresorcinol (m. p. 175.5°C), also known as styphnic acid, is a yellow crystalline product which dyes animal fibres intensely. 100 ml of water dissolves 0.641 g of it at 14°C, and 1.136 g at 62°C.

More recent solubility data by Aubertein and Emeury [29] are: in 100 g of water 0.45 g of styphnic acid are soluble at 15°C 0.55-0.58 g at 20°C 0.68-0.69 g at 25°C.

Knox and Richards [30] determined the solubility of styphnic acid in nitric acid of various concentrations at 25°C, expressed as the "normality" of the HNO_3 solutions. Aubertein and Emeury have recalculated their results expressing the solubility in a more convenient way:

HNO_3, wt. %	0	10.67	41.91	55.9	69.57
Solubility in 100 g of the acid, g	0.53	0.034	0.125	0.32	1.37

Aubertein and Emeury have also determined the solubility of styphnic acid in sulphuric acid of different concentrations at 25°C:

H_2SO_4, wt. %	0	6	20	50	80	92
Solubility in 100 g of the acid, g	0.65	0.07	0.01	0.10	0.13	0.13

The solubility of styphnic acid in nitric acid-sulphuric acid mixtures is very low.

Aubertein and Emeury examined the solubility in a spent acid mixture of the composition :

HNO_3	10%
H_2SO_4	72%
H_2O	18%

At room temperature it is below 0.005%. At 35-40°C the solubility is below 0.01%, and at 80°C it is below 0.1%.

Styphnic acid is slightly hygroscopic. It absorbs 2-3% of water after being exposed for 30-100 hr at an atmosphere of 60% humidity at 25°C [29].

Styphnic acid is readily soluble in glycol diacetate : 100 g of the solvent at 20-25°C can dissolve about 13 g of the substance.

Chemical properties

Trinitroresorcinol, like other compounds of this type, forms addition compounds with aromatic hydrocarbons. Some of them investigated by Jefremov [24], containing the two components in the molar ratio of 1:1, are listed below:

	melting point, °C
with naphthalene	165.5
„ acenaphthene	156.0
„ anthracene	176.3
„ phenanthrene	132.7
„ retene	135.7

With chloro- and bromo-naphthalenes it yields compounds melting within a wide temperature range.

With regard to explosive power and sensitiveness trinitroresorcinol is similar to picric acid. Since its price is considerably higher than that of picric acid it is not used in explosive technology. Only lead trinitroresorcinate is of great practical importance as an initiator (Vol. III). On the whole the properties of trinitroresorcinol salts are similar to those of picrates.

Purity

The purity of the product depends on the method of carrying out the reaction. The melting point of the product prepared by Aubertein and Emeury [29] was 176.2-176.5%.

However, high purity of styphnic acid is not required when the substance is used to produce the lead salt by the continuous method according to Meissner (Vol. III). Some manufactures claim to achieve better results with an impure brown product of low melting point - max. 170°C.

Styphnic acid of low purity can be obtained by sulphonating resorcinol with spent sulphuric acid or by sulphonation with sulphuric acid added with sodium nitrite according to the method of Wilkinson [31].

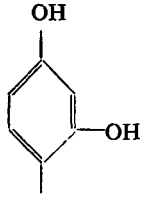
Wilkinson's method has been studied by Aubertein and Emeury [29]. They found that the yield of the product is reduced when the proportion of nitrite is increased, and the rate of reaction is diminished. A relatively high proportion of nitrite (2-4%) in the sulphonating acid considerably increases foaming during nitration. The quantity of sodium nitrite should, therefore, be kept within the limits of l-2%. A temperature of 50-55°C should be maintained at the beginning of nitration. Increasing the temperature by 1.5°C reduced the yield by 1%.

The product thus obtained has a chestnut brown colour and m. p. 165-168.5°C depending on the proportion of nitrite used.

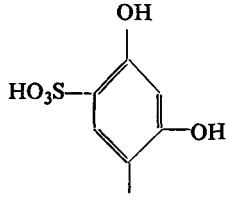
Method of preparation

Trinitroresorcinol is usually prepared by a method which consists in the sulphonation of resorcinol to disulphonic acid which is then nitrated. The process comprises two stages: sulphonation and nitration.

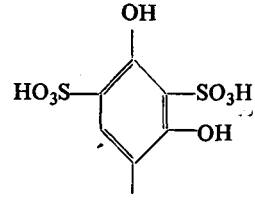
Sulphonation yields only three compounds: I, II, and III.



I



II



III

The sulphonic acids I and II can be obtained by sulphonation of resorcinol with sulphuric acid or oleum at temperatures which are not higher than 100°C (Mertz and Zetter [32]). The trisulphonic acid can only be prepared by the action of oleum at 200°C. According to Aubertein and Emeury [29], resorcinol can be sulphonated to the compound II by the action of a tenfold quantity (by weight) of sulphuric acid of concentration 92-97.5% H_2SO_4 or oleum (105% H_2SO_4) at 50°C. However, a small proportion (1%) of resorcinol remains unchanged and is subjected to oxidation during the subsequent nitration. It is responsible for foaming during the nitration. According to the above authors, prolonged sulphonation or application of more concentrated oleum does not prevent the presence of unsulphonated resorcinol.

Nitration can be achieved by acting with nitric acid (50-90% HNO_3) on sulphonated resorcinol partly dissolved and partly suspended in the excess of sulphuric acid (Mertz and Zetter [32]), keeping the temperature below 55°C on mixing ihe reagents and raising it to 80°C by the end of the reaction.

All who have carried out this reaction in practice know that during nitration foaming occurs and sometimes makes the process impossible on a larger scale. Strong foaming also means the formation of very fine crystals of styphnic acid difficult to filter.

Aubertein and Emeury [29] made a detailed examination of the causes of foaming. Oxidation of non-sulphonated resorcinol is the original cause of gas evolution during nitration. When the product is in the form of very fine crystals the gas bubbles attach themselves to the crystals and raise the product to the surface in the form of a foam. This does not occur when the crystals of the product are large. Therefore, the method of nitration should be such as to favour formation of large crystals of styphnic acid. To achieve this, Aubertein and Emeury advise:

(1) keeping the temperature of nitration constant and avoiding any fall in temperature;
(2) keeping the concentration of nitric acid during the nitration as constant as possible and the temperature near to 55°C;
(3) avoiding the application of too vigorous stirring particularly just before the styphnic acid begins to crystallize. Excessive stirring promotes foaming.

Aubertein and Emeury established the influence of various other factors upon the fineness of crystals and subsequently on the foaming. For example a lower concentration of sulphuric acid (92-97%) used for sulphonation favours the formation of fine crystals and hence of foam. This is the result of a low rate of nitration produced by the lower concentration of the nitrating acid.

The yield of styphnic acid depends on the excess of nitric acid. It falls from 86 to 82% of theoretical when the excess is reduced from 45 to 14%.

Styphnic acid of high purity

Sulphonation. 100 parts of resorcinol are introduced in small increments during a period of half an hour into 1000 parts of sulphuric acid (93-98%) under stirring. The temperature rises to 50°C and is maintained then for 15 min, when the mixture is ready to be nitrated.

Nitration. 200 parts of concentrated nitric acid (90% HNO_3) are added to the sulphonation mixture in such a way that the first 110 parts are introduced relatively quickly (within 30-50 min), and the temperature is kept between 50° and 55°C. After that, the rate of stirring and the rate of introducing nitric acid is reduced (3-5 times) to maintain the temperature at 55-60°C. Styphnic acid begins to crystallize. From this moment the rate of adding nitric acid is gradually increased and cooling is so arranged that the temperature finally reaches 60-65°C.

The whole is stirred for half an hour at this temperature, cooled, filtered, washed with cold water until the wash water is neutral to Congo paper and dried at 60°C.

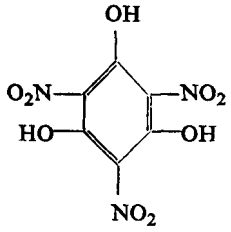
The yield of the product with m. p, 176°C is 180-185 parts.

Styphnic acid of low purity

Sulphonation. 10-20 parts of sodium nitrite are added to 1000 parts of sulphuric acid (92-98%) and 100 parts of resorcinol are introduced as above.

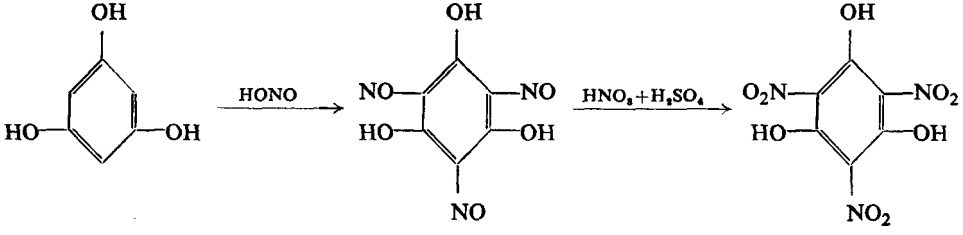
Nitration. Initially 125 parts of nitric acid (instead of 110 parts) are added. Otherwise the process is the same as described above.

TRINITROPHLOROGLUCINOL

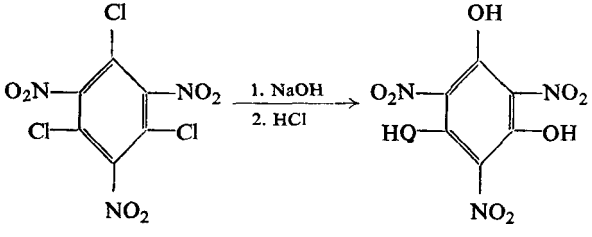


Trinitrophloroglucinol (m. p. 167°C) has not found any practical application, although several authors have proposed using trinitrophloroglucinol salts, primarily its lead salt, as an initiator (e.g. Friedrich [33]; Rathsburg [34]; Sorm and Drapalova [35]; T. Urbariski and Kruszyriska [36]).

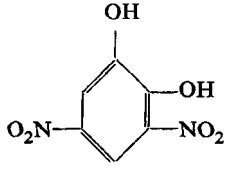
Trinitrophloroglucinol may be obtained in various ways, e.g. from phloroglucinol by nitrosation, followed by oxidation with nitric acid (Benedikt [37]):



or from trichlorotrinitrobenzene by boiling with a sodium hydroxide solution (Sorm and Drapalova [35]):



DINITROPYROCATECHOL



3,5-Dinitropyrocatechol (m. p. 164°C) was prepared by Nietzki and Moll [38] by nitrating pyrocatechol diacetate with cold cont. nitric acid, followed by hydrolysis of ester groups with sulphuric acid.

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CHAPTER XVI

PICRIC ACID ETHERS

As an explosive the acidic character of picric acid and its readiness to form picrates are serious drawbacks. In an attempt to eliminate these disadvantages the substitution of the acid hydrogen by an aliphatic or aromatic radical has been suggested. The compounds thus formed would be picric acid ethers. For the substitution of hydrogen by aromatic radicals the latter were connected with nitro groups.

Maxim [1] and du Pont de Nemours Inc. [2] were the first to suggest the application of the methyl ether, trinitroanisole, as an explosive.

During World War I materials of this type were used fairly extensively. However, it has been proved that some of them can undergo hydrolysis, yielding free picric acid, thus rendering any further use of such explosives unjustifiable. In addition, most of the products have strongly toxic properties. Hence during World War II compounds of this type were used only on a small scale.

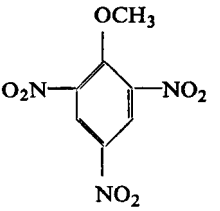
During the 1914-1918 War trinitroanisole was manufactured in Germany under the names of Nitrolit, Trinol and An. It was used alone or in admixture with ammonium nitrate, hexyl, or hexanitrodiphenyl sulphide, for filling high explosive shells and for submarine and land mines. Eventually it had to take the place of TNT.

In France trinitroanisole was made use of only on the semi-commercial scale, in mixtures with picric acid or with ammonium or sodium nitrate for filling bombs. During World War II trinitroanisole was manufactured in Japan for tiling armour piercing shells.

Trinitroanisole was first obtained by Cahours [2a] by the direct nitration of anisole. The reaction proceeds very vigorously, as the presence of a methoxy group greatly facilitates the introduction of nitro groups and some highly coloured by-products are formed [20]. For this reason it is preferable to prepare trinitroanisole via chlorodinitrobenzene (p. 547).

Similarly trinitrophenetole was first obtained by the direct nitration of phenetole, but at present this method is not used, chlorodinitrobenzene being a starting material. Trinitrophenetole is less important then trinitroanisole. Its manufacture never developed beyond the semi-commercial scale. Similarly other picric acid ethers, as for example nitro derivatives of phenyl ether, have not found any practical use.

TRINITROANISOLE

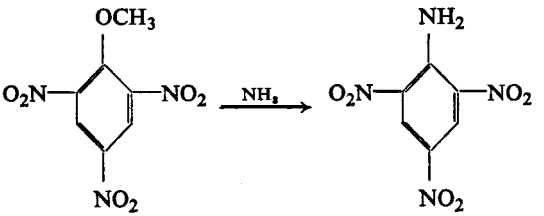


2,4,6-Trinitroanisole (m. p. 67°C) forms white needles (sp. gr. 1.408), very difficult to dissolve in water: at 15°C 100 ml of water dissolve only 0.02 g and at 50°C 0.137 g of trinitroanisole. The product is sparingly soluble in carbon disulphide and carbon tetrachloride, relatively easily soluble in alcohol and still more so in ether, benzene, chloroform and ethyl acetate.

CHEMICAL PROPERTIES

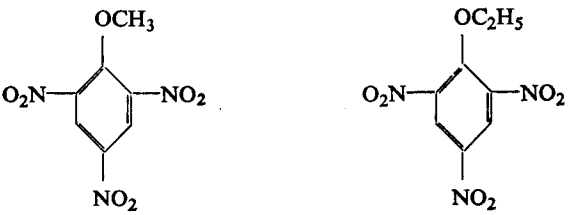
By the action of alkalis trinitroanisole is hydrolysed slowly in the cold and more rapidly in the hot, forming the corresponding picrates (Salkowski [3]). It also undergoes slow hydrolysis under the influence of water, picric acid being formed. Hydrolysis may take place even in the presence of moisture in the air, so that trinitroanisole may in the course of time form picrates.

The methoxy group is rather reactive and may be substituted. For example, boiling with ammonia leads to the formation of trinitroaniline:



(1)

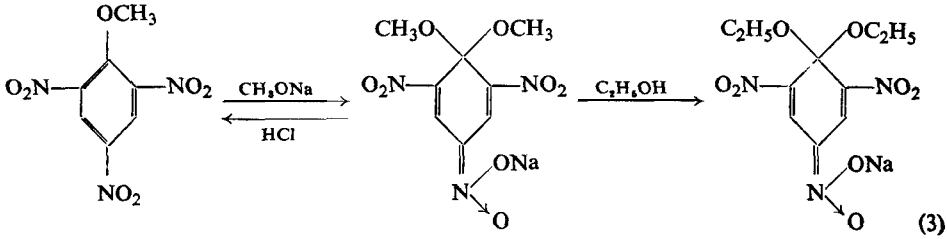
When boiled with ethyl alcohol trinitroanisole is converted to trinitrophenetole:



(2)

It is, therefore, necessary to use methyl alcohol as the solvent for the recrystallization of trinitroanisole.

With sodium- or potassium methoxide, trinitroanisole reacts like sym-trinitrobenzene or α– trinitrotoluene, viz. it adds on an alcoholate molecule, forming a red-coloured addition product (I) :



(3)

I II

The quinonoid structure (see p. 202) is assigned to this product. It decomposes by the action of acids to yield trinitroanisole again. Boiling with ethyl alcohol converts the addition product into the analogous derivative of phenetole and sodium ethoxide (II).

TOXICITY

Trinitroanisole is highly toxic. According to Ilzhijfer [4], poisoning by this substance causes headache, weakness, loss of appetite, gastric disturbances and irritation of the mucous membrane of the upper respiratory tract. Its action on the skin is particularly harmful. It causes redness, peeling and in more severe cases blisters, which may join and burst, giving wounds that are difficult to heal. The sensitivity of individuals differs greatly. Inhaling the dust should be avoided. Protective clothing and a daily bath after work are highly recommended for those working with the material. Bare parts of the skin should be protected by a neutral, weakly absorbent ointment, as for example Vaseline (Lazarev [5]).

EXPLOSIVE PROPERTIES

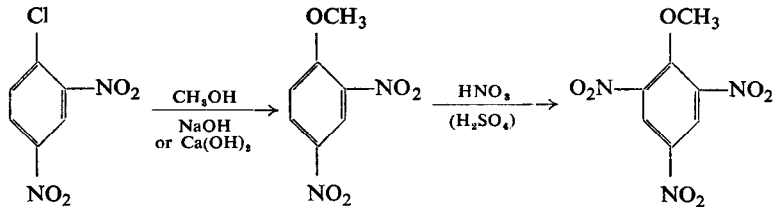
Dry trinitroanisole is very stable: heating at 95°C for 24 hr leaves it unaffected. It is distinctly less sensitive to impact than picric acid - the impact energy figure for explosion produced by a falling weight amounts to 124-129% of that for picric acid. Its explosive power is slightly less than that of picric acid. Desvergnes [6] gave the following comparative values determined in a manometric bomb for densities of loading d = 0.20 and 0.25 g/cm^3.

trinitroanisole	A = 0.20 g/cm^3	2145-2222 kg/cm^2
	A = 0.25 g/cm^3	2850 kg/cm^2
picric acid	A = 0.20 g/cm^3	2210-2310 kg/cm^2
	A = 0.25 g/cm^3	3230 kg/cm^2

The maximum rate of detonation is 7640 m/sec at a density of 1.60 g/cm^3.

MANUFACTURE OF TRINITROANISOLE

In industrial practice a process based on the following reaction:



(4)

is used.

In a Japanese factory at Maizuru a two stage process was used for the manufacture of trinitroanisole, namely: alcoholysis of 1-chloro-2,4-dinitroberuene to 2,4-dinitroanisole and subsequently nitration of di- to tri-nitroanisole.

Alcoholysis of 1-chloro-2,4-dinitrobenzene to 2,4-dinitroanisole. To 800 kg of methyl alcohol in the reactor 196 kg of sodium hydroxide and 600 kg of chlorodinitrobenzene are added in 10 equal portions. The reagents are added alternately. During this operation, which requires 7 hr, a temperature at 40-45°C is maintained. Then the temperature is raised to 50°C by heating the reactor jacket and kept there for 30 min, before cooling the whole mixture to 35°C (which takes 3 hr). The crystals of the product together with the mother liquor are then transferred to a vacuum filter for separation. The product obtained is washed four times with water, centrifuged and finally transferred to the nitration plant.

Some 550 kg of dinitroanisole can be obtained, i.e. the yield is 95% of the theoretical.

Nitration of di- to tri-nitroanisole. A conventional type of a nitrator, with a jacket for cooling or heating, but without a coil is used. 3200 kg of a mixture of acids :

HNO_3	17%
H_2SO_4	77%
H_2O	6%

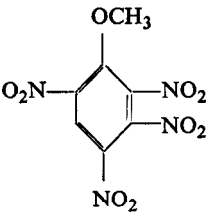
is charged into the nitrator. The mixture is prepared by fortifying the spent acid.

550 kg of dinitroanisole is hand-fed to the nitrator, which requires 6 hr. The temperature is allowed to rise to 50-55°C and is maintained there during the operation. The nitrator contents are then heated to 60-68°C and kept at this temperature for half an hour before being cooled to 35°C. This takes another 4 hr. The trinitroanisole formed is separated from the acid on a filter. The spent acid is fortified with nitric acid (sp. gr. 1.50) and is *m-* used for nitration. The product is washed five times with water which is subsequently removed by centrifuging. In this way 615-620 kg of trinitroanisole is obtained, which is 93% of the theoretical yield.

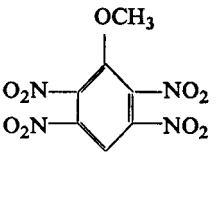
Purification of trinitroanisole. In the past trinitroanisole was purified by dissolving in methyl alcohol. The solution was filtered and the product precipitated by introducing the solution into water. Later the purification process was simplified, the crude trinitroanisole being agitated with hot water, the water decanted

and cold water added to the molten product with constant stirring. In this way granules of trinitroanisole are obtained. They may be separated from water by filtration or centrifugation.

TETRANITROANISOLE



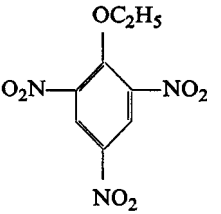
m. p. 94°C



m. p. 151°C

A mixture of the tetranitroanisole isomers may be obtained (according to Claessen [7]) by the nitration of *m*- nitroanisole. The compounds are not stable since their nitro groups in the *meta* position are readily hydrolysed or substituted (van Duin and van Lennep [8]). Their sensitiveness to impact is similar to that of TNT. The expansion they give in a lead block is about 135% of that given by TNT.

TRINITROPHENETOLE



The physical and chemical properties of trinitrophenetole (m. p. 78°C) are similar to those of trinitroanisole. Thus, for example, on the prolonged action of water it undergoes hydrolysis, and its OC_2H_5 group can easily be replaced by an amino group.

By crystallization from methyl alcohol trinitrophenetole is converted into trinitroanisole. It also adds on a molecule of sodium or potassium alcoholate to form a bright coloured salt.

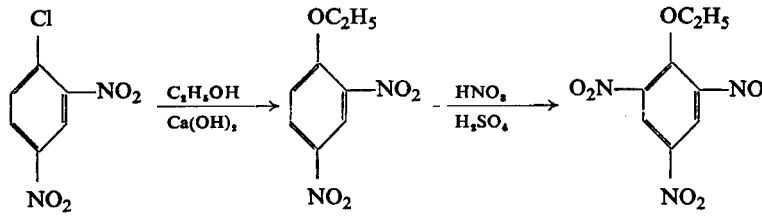
Trinitrophenetole may be exploded by an impact energy amounting to 120% of that required for picric acid. With regard to its explosive power, trinitrophenetole is somewhat weaker than trinitroanisole. Measurements in a manometric bomb by Desvergnes [5] gave the following results:

at a density of loading A = 0.20 g/cm^3 pressure produced was 1774 kg/cm^2
A = 0.25 g/cm^3 „ „ „ 2490 kg/cm^2
A = 0.3 g/cm^3 „ „ „ 3318 kg/cm^2

(see p. 546)

It gives a lead block expansion equivalent to 84% of that produced by picric acid. Its rate of detonation, however, is relatively high - its maximum value being 6880 m/sec.

Trinitrophenetole is prepared in a way similar in principle to that for trinitroanisole :



(5)

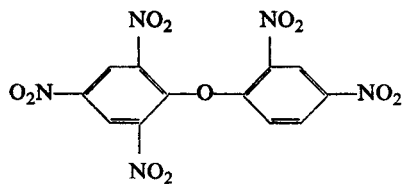
The greatest difficulty to overcome is the nitration of dinitrophenetole to trinitrophenetole, since it must be carried out within a narrow temperature range. Too high a temperature may result in a decomposition of the product, while too low a temperature causes a considerable part of the substance to remain unnitrated. Nitration at 60°C gives the best results.

POLYNITRO DERIVATIVES OF DIPHENYL ETHER

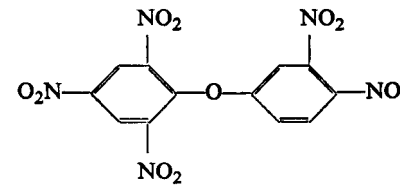
Polynitrodiphenyl ethers (for example hexanitro-) cannot be obtained by the direct nitration of diphenyl ether. Therefore attempts have been made to prepare the polynitro compounds (beginning with the pentanitro compounds) by indirect ways.

PENTANITRODIPHENYL ETHER

Two isomers of pentanitrodiphenyl ether are known:

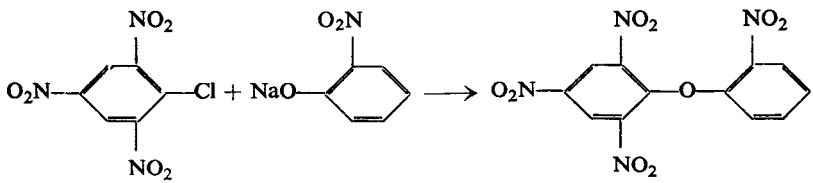


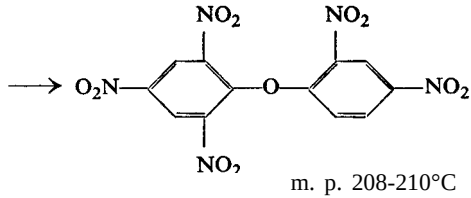
I



II

Isomer I (2,4,6,2',4'-, m. p. 210°C was obtained by Desvergnes [6] by reacting picryl chloride with sodium *o*- nitrophenate, followed by the nitration:



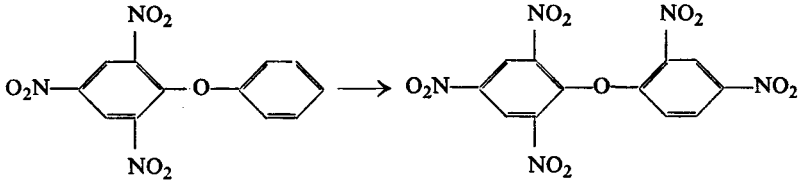


(6)

m. p. 208-210°C

An attempt to introduce one more nitro group so as to obtain symmetric picryl oxide failed, since under the necessary vigorous nitration conditions decomposition of the product took place.

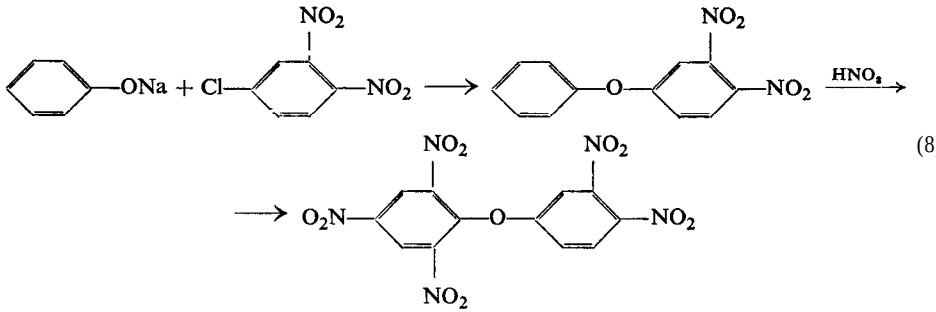
According to Okon [9], compound I may be obtained by the nitration of 2,4,6-trinitrodiphenyl ether (III), which in turn is formed by the action of phenol on picryl-pyridinium chloride (p. 464) :



(7)

III (m. p. 155-156°C) I

Isomer (II) 2,4,6,3',4'-pentanitrodiphcnyl ether (m. p. 200°C) is usually prepared by a Westfalisch-Anhaltische Sprengstoffe A. G. method [10], based on the reactions:

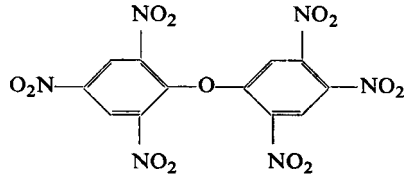


(8)

Neither substance is a strong enough explosive to make their rather expensive production economical.

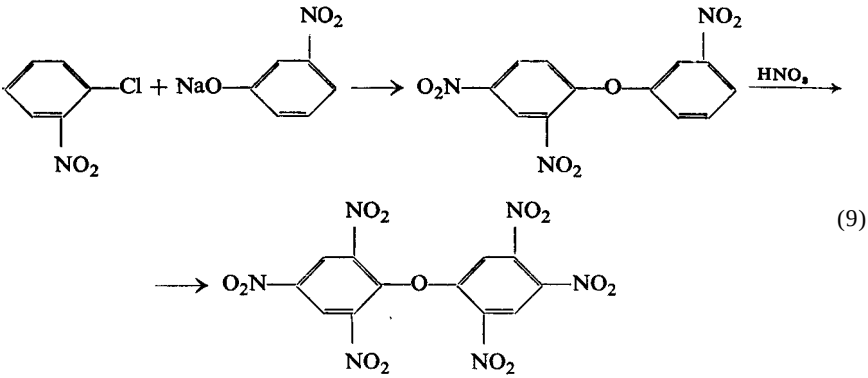
HEXANITRODIPHENYL ETHER

Only unsymmetrical 2,4,6,3',4',6'-hexanitrodiphenyl ether (VI) melting at 278°C (269°C) is known.



IV

It may be prepared by a method described in the patent filed by Westfälisch-Anhaltische Sprengstoffe [10], namely :



(9)

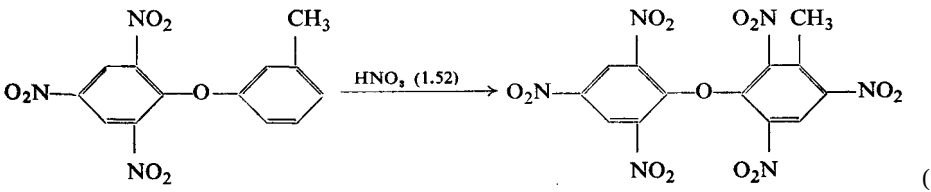
IV

The authors state that the substance is less sensitive and more powerful than picric acid.

This was not confirmed by van Duin and van Lennep [8] who found the sensitivity of hexanitrodiphenyl ether to be higher than that of tetryl. The same authors determined the initiation temperature to be 318°C. Neither is the stability of the product satisfactory, since after 8 hr heating at 95°C the evolution of nitrogen oxides may be observed.

According to data reported in the literature, sym-hexanitrodiphenyl ether should be considered as an unstable compound and it is to this fact, that the failure to obtain it is usually ascribed.

Recently Okori and Grabowski [ll] have proved that the whole system can be stabilized by the presence of a methyl group on one of the benzene rings, in the *meta* position to the ether bond. The stable compound VI can be obtained by nitrating *m*- cresylpicric ether (V) with pure (100%) nitric acid:



(10)

V

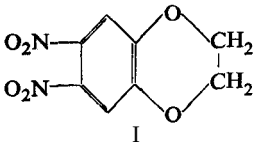
VI

m. p. 220-222°C

NlTRO DERIVATIVES OF VARIOUS PHENOLIC ETHERS

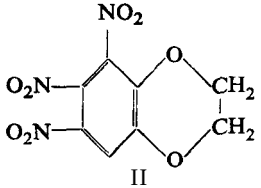
Polynitro derivatives of the simplest cyclic ether of pyrocatechol-1,2-ethylenedioxybenzene are interesting because of the position of the nitro groups (Vor-Kinder [12]).

They are di-, tri- and tetra-nitro compounds (I), (II) and (III) respectively:



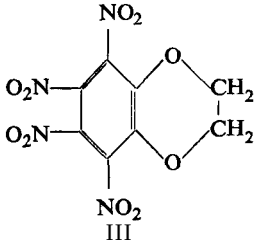
I

m. p. 132-134°C



II

m. p. 156°C

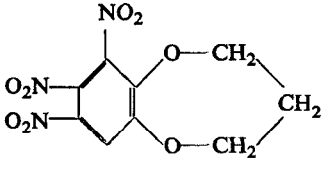


III

m. p. 286°C

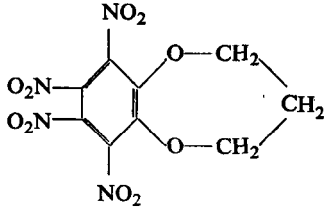
(G. M. Robinson and R. Robinson [13], Gosh [14], Heertjes, Dahmen and Wierda [11).

Hackel and Kuboszek [16] prepared tri- and tetra-nitro derivatives of l,2-propylenedioxybenzene, (IV) and (V) respectively:



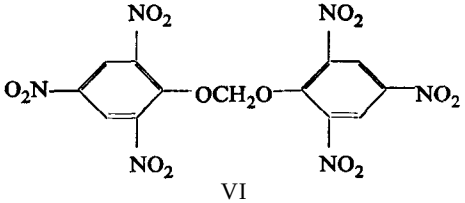
IV

m. p. 170°C



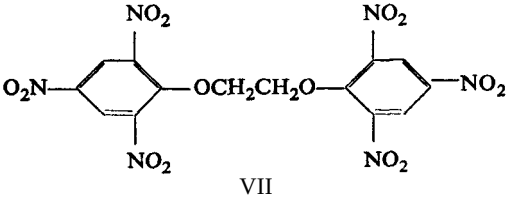
V

m. p. 185°C



VI

m. p. 105-107°C



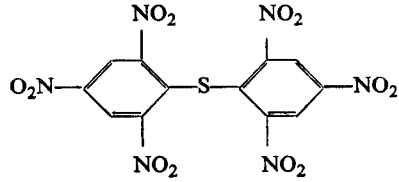
VII

m. p. 196-197°C

The two compounds VI and VII were prepared by nitrating methylene- and ethylene-diphenyl ethers respectively (Stefanovic and Ciric [16a]).

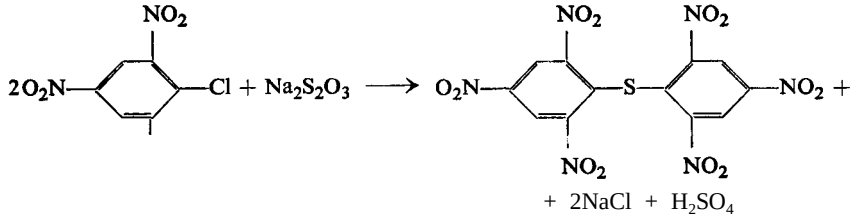
HEXANITRODIPHENYL SULPHIDE

Only one representative of this group is known in industrial practice, namely hexanitrodiphenyl sulphide (picryl sulphide, hexasulphide, Hexide) of melting point 234°C.



2,2',4,4',6,6'-Hexanitrodiphenyl sulphide forms golden crystals, difficult to dissolve in most organic solvents.

The compound was first obtained by Sprengstoff A. G. Carbonit [17], in 1912, from picryl chloride and sodium thiosulphate in alcoholic solution in the presence of magnesium carbonate for binding the sulphuric acid which forms in the reaction:



(11)

The yield obtained is about 90% of the theoretical. According to Giua [18], thiourea may be used in place of sodium thiosulphate.

The compound may also be prepared from picryl-pyridinium chloride (see p. 464).

The product does not colour the skin and, according to the German literature, is not toxic. However, Roche and V. Thomas [19] reported its vapour to be strongly irritant. During World War I the Germans used picryl sulphide in mixtures with TNT, with or without ammonium nitrate, for filling bombs.

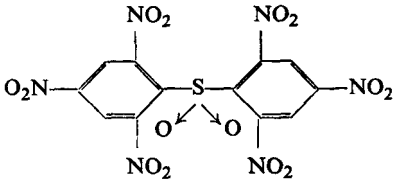
Since the explosive decomposition of picryl sulphide and of its mixtures yields SO_2 among other decomposition products, the compound has been proposed for filling shells to be used against confined objectives, such as ships' interiors, bunkers, etc. As a result of explosion a noxious atmosphere containing SO_2 would result.

Picryl sulphide is a stable explosive. Van Duin and van Lennep [8] found its initiation temperature to be 302-319°C depending on the rate of heating. When kept at 95°C for 30 days the substance remained unchanged.

Its sensitiveness to impact is somewhat lower than that of tetryl, but higher than that of hexyl or picric acid.

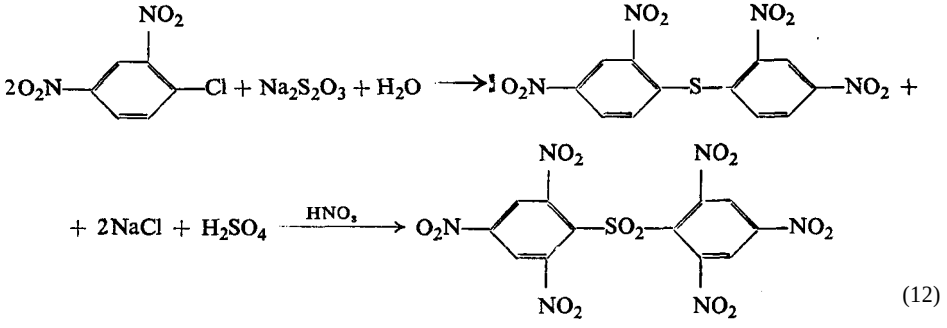
The lead block expansion given by picryl sulphide is equal or, according to some authors, slightly larger than that given by picric acid (325-350 cm^3).

HEXANITRODIPHENYL SULPHONE



2,2',4,4',6,6'-Hexanitrodiphenyl sulphone (m. p. 307°C, decomposition) forms yellowish crystals difficult to dissolve in most organic solvents.

In 1912 Sprengstoff A. G. Carbonit [17] was granted a patent for a method of preparation of this explosive, consisting in reacting hexanitrodiphenyl sulphide with nitric acid. Since picryl chloride, as the starting material for picryl sulphide was rather expensive, another method of preparation of hexanitrodiphenyl sulphone, via tetranitrodiphenyl sulphide, was also used. The latter was obtained by treating chlorodinitrobenzene with sodium thiosulphate. Then it was nitrated and oxidized simultaneously with nitric acid to hexanitrodiphenyl sulphone:



(12)

During World War I the compound was used by the Germans in mixtures with TNT and sometimes also with ammonium nitrate for filling bombs.

Hexanitrodiphenyl sulphone proved to be a stable compound. According to van Duin and van Lennep [8], it withstands heating at 95°C for 30 days. Its initiation temperature is 297-308°C depending on the rate of heating.

It is a more powerful explosive than hexyl or picryl sulphide, mainly due to a more favourable oxygen balance, and also surpasses picric acid. Its sensitivity to impact is of the order of tetryl.

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CHAPTER XVII

NITRO DERIVATIVES OF ANILINE

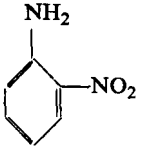
APART from tetryl, which is discussed in the chapter on nitramines (Vol. III), the only aniline nitro derivative that has gained any considerable importance as an explosive is hexanitrodiphenylamine, or hexyl. None of the other nitro derivatives has proved of greater interest: though some achieved temporary importance (as for example tetranitroaniline) or aroused a theoretical interest.

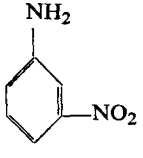
The introduction of nitro groups to a compound containing a NH_2 group presents some difficulties, because of the high reactivity of this group and because of the readiness of such compounds to undergo oxidation. Therefore, a nitro group should be introduced into aniline or its homologues (other than N-substituted) only after the amino groups had been protected by acylation, for example to acetanilide.

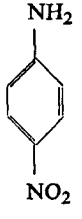
A more modem method of preparation of nitroaniline derivatives consists in using chlorodinitrobenzene as starting material. Advantage is taken of the reactivity of its chlorine atom which can be substituted by an amino group.

MONONITRO DERIVATIVES OF ANILINE

Three isomeric nitroanilines: ortho- (m. p. 71.5°C), *meta*- (m. p. 114°C) and *para*- (m. p. 148°C) are known.







Para-nitroaniline was obtained by A. W. Hofmann [1] who nitrated acetanilide to *p*- nitroacetanilide which was then hydrolysed with a sodium hydroxide solution.

Khmer [2] found that acetanilide when nitrated also yields *o*- nitroacetanilide, from which *o*- nitroaniline may be obtained by hydrolysis. The nitration of acetanilide

had been applied for a long time as a commercial method of preparation of *o*- and *p*- nitroanilines and was investigated by a number of authors including Beilstein and Kurbatov [3] and Holleman [4]. The mononitation of acetanilide can be effected even with 80% nitric acid.

Walker and Zincke [5] found that *o*- and *p*- nitroanilines could be obtained by heating corresponding bromonitro derivatives of benzene with ammonia under elevated pressure. The high yield of the reaction was due to the enhanced reactivity of Br in the presence of the nitro group. The reaction has been utilized for the commercial preparation of *o*- and *p*- nitroanilines. *Ortho*- or *p*- chloronitrobenzenes are used as starting material.

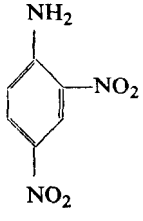
Meta- nitroaniline was first prepared by Muspratt and A. W. Hofmann [6] in 1846, by the reduction of *m*- dinitrobenzene with ammonium sulphide. Nowadays with sodium sulphide used as reducing agent, this method is applied for the commercial production of *m*- nitroaniline.

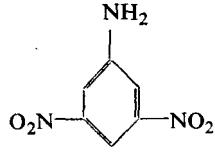
Nitroanilines may also be obtained by direct nitration of aniline (Bruns [7]), provided that a solution of aniline sulphate in sulphuric acid is prepared first, and then carefully introduced into a mixture of nitric acid with concentrated sulphuric acid. A condition necessary for success is that the reaction temperature must not exceed 0°C.

Among the three isomeric nitroanilines only *m*- nitroaniline was of any importance in explosives technology, being a starting material for the preparation of tetranitroaniline.

DINITRO DERIVATIVES OF ANILINE

From among a number of dinitroaniline isomers known, only the 2,4- and 3,5-isomers (m. p. 187°C and 161°C respectively) are of importance from the point of view of explosives chemistry:





2,4-Dinitroaniline forms yellow needles, difficult to dissolve in cold alcohol. The compound was obtained by Rudnev [8] by vigorous nitration of acetanilide to 2,4-dinitroacetanilide with an almost anhydrous nitrating agent, followed by hydrolysis of the product.

Nowadays 2,4-dinitroaniline is prepared on a large scale by treating chlorodinitrobenzene with ammonia. The method was first reported by Engelhardt and Lachinov [9] in 1870. Heating 2,4-dinitrophenol with an excess of urea at 208°C

(Kym [10]) is another convenient method of preparation of 2,4-dinitroaniline. Further nitration of 2,4-dinitroaniline leads to 2,4,6-trinitroaniline (picramide).

3,5-Dinitroaniline is usually obtained from 1,3,5-trinitrobenzene by reduction of a nitro group with sodium hydrosulphide. It may be used as starting material for the preparation of pentanitroaniline.

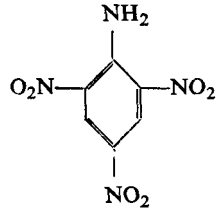
2,4-Dinitroaniline has weak explosive properties of the order of *m*- dinitrobenzene. However, its sensitivity to impact, according to Wöhler and Wenzelberg [10] is considerably higher than that of dinitrobenzene and similar to that of TNT.

The manufacturing process applied for the production of 2,4-dinitroaniline at I. G. Höchst was as follows:

To 1700 1. of water 600 kg of chlorodinitrobenzene (m. p. not below 50°C) are added while stirring, followed by 530 1. (480 kg) of 26.5% aqueous ammonia. The whole is kept at 70°C for 2 hr. When the reaction has started the steam flow must be stopped for a while since the temperature rises spontaneously to 115-120°C (within 152 hr) due to the heat of the reaction. The pressure in the reactor rises to 2 atm. After the temperature has become constant, steam is passed again to keep the reactor contents at this temperature for another 4 hr. The temperature should not exceed 130°C.

Then the reaction mixture is cooled while stirring, the precipitated product is filtered off on a stoneware filter, washed with water until neutral and dried in a shelf drier at 50°C for 12-16 hr. The product is obtained in almost theoretical yield.

TRINITROANILINE (PICRAMIDE)



Picramide or 2,4,6-trinitroaniline (m. p. 190°C) forms deep yellow crystals, difficult to dissolve in alcohol and ether but easily soluble in hot acetone, benzene and ethyl acetate.

The compound was first obtained by treating picryl chloride (Pisani [12]) or trinitroanisole with ammonia (Salkowski [13]). Later Witt and Witte [14] obtained it by the nitration of *o*- or *p*- nitroacetanilide in oleum solution. For the nitration a solution of KNO_3 in concentrated sulphuric acid was used. Spencer and Wright [15] applied Kym's method [lo] for the preparation of picramide, heating picric acid with urea at 173°C for 36 hr. The yield obtained was about 90% of the theoretical.

CHEMICAL PROPERTIES

Like most polynitro-aromatics, picramide forms addition compounds with condensed ring aromatic hydrocarbons. Compounds containing their constituents in 1:1 molecular proportion include those with:

	melting point, °C
naphthalene, orange crystals	168-169
anthracene, red crystals	165-170
aniline, dark red crystals	123-125
dimethylaniline, dark blue crystals	139-141

By thermoanalysis Jefremov [16] found that similar compounds, also in the molecular proportions of 1:1, were formed by picramide with:

	melting point, °C
acenaphthene	195.4
phenanthrene	160.2
retene	125.1
fluorene	(non-uniformly melting)

According to Jefremov, picramide forms eutectics with:

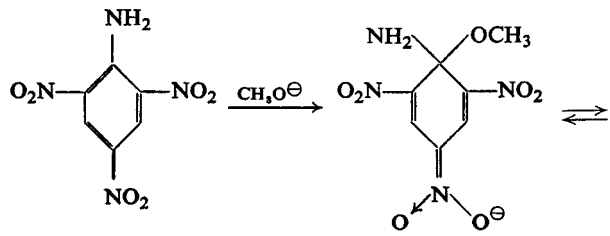
	melting point, °C
11.5% of picric acid	113.5
15.9% of tetryl	110.8
76.5% of trinitroxylene	110.8

Picramide may be used for the preparation of tetranitrobenzene (p. 257). Boiling picramide with a sodium hydroxide solution results in its hydrolysis, picric acid and ammonia being formed. This is due to an action of nitro groups on the amino group.

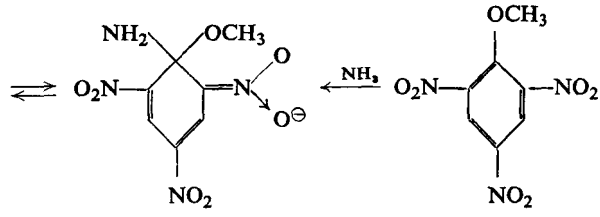
Picramide reacts with sodium methoxide in the same manner as trinitrobenzene, forming coloured solutions. Some solid salts have been prepared by Busch and Kögel [17]. Recently Farmer [18] found that the coloured compound I can be obtained by two methods:

(a) by the action of methoxides on trinitroaniline;

(b) by the action of ammonia on trinitroanisole:



Ia

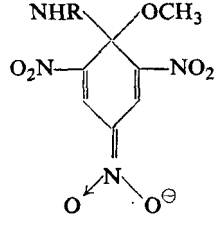


(1)

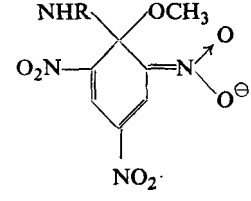
Ib

Acidification of I regenerates picramide.

If instead of ammonia a primary amine NH_2R is used N-substituted picramides are formed through an intermediate IIa or IIb:

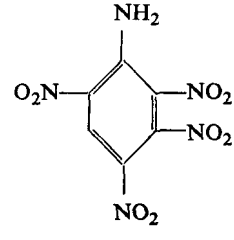


IIa



IIb

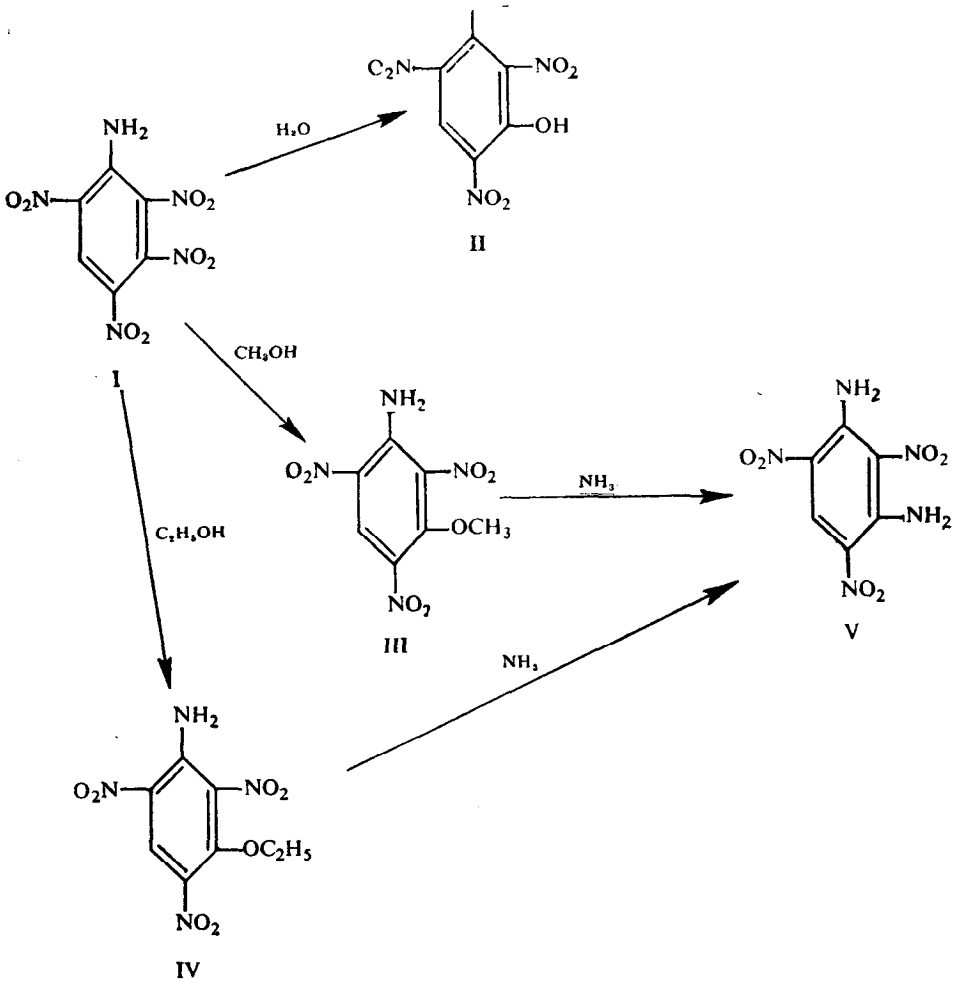
TETRANITROANILINE



2,3,4,6-Tetranitroaniline (m. p. 215°C, decomposition) is a yellowish crystalline substance, difficult to dissolve in most of organic solvents but soluble in acetone (17 parts in the boiling solvent) and *o*- nitrotoluene (some 33 parts at 140°C).

Tetranitroaniline was first obtained by Flürscheim [19, 19a], who proposed its use as an explosive because its properties were similar to those of tetryl. For the preparation of tetranitroaniline Flürscheim nitrated *m*- nitroaniline with a mixture of concentrated acids at 70-80°C. The yield was 64-69% of the theoretical (from 100 kg of *m*- nitroaniline only 130-140 kg instead of 204 kg could be obtained).

Tetranitroaniline is a rather unstable compound. Thus, when boiled with water its *meta*- nitro group undergoes hydrolysis to a phenolic group (II), while on boiling with methyl- or ethyl alcohol it yields an anisole- (III) or phenetole derivative (IV), which with ammonia may form trinitro-m-phenylenediamine (V):



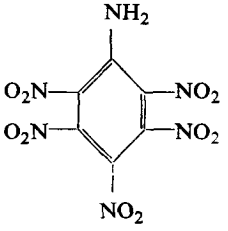
Although, according to Flürscheim, tetranitroaniline has sufficient thermal stability, even a product of the highest purity does not give a satisfactory heat test.

According to Ingraham [19b], tetranitroaniline has shown evidence of decomposition by the heat test at 65.5°C when only a small amount of moisture was piesent. The main product of decompositions was II. Prolonged heating at 75°C results in loss of a nitro group. At 120°C decomposition takes place which proceeds in a way similar to that of tetryl. The initiation temperature is 231-233°C. The specific gravity of the product is 1.867 [19].

With regard to explosive power and sensitiveness to impact tetranitroaniline does not differ from tetryl. However, because of its poor stability it has not found any practical use.

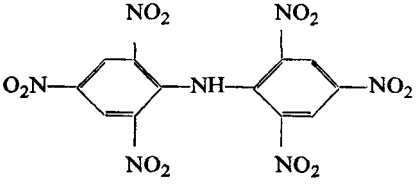
Tetranitroaniline may be utilized as starting material for the preparation of stable compounds II, III and V. However, none of them exhibits any properties which would justify the high costs of their application as explosives.

PENTANITROANILINE



Flürscheim and Holmes [20] obtained pentanitroaniline (m. p. 238°C, decomposition) by the nitration of 3,5-dinitroaniline (p. 557). The product has proved to be a powerful explosive, of the order of penthrite or hexogen. However, its nitro groups located in the 3- and 5-positions can readily be split off or substituted, making the compound insufficiently stable for use as an explosive.

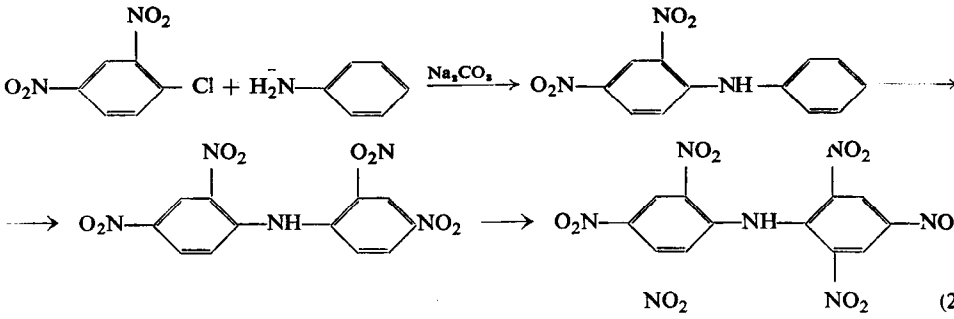
HEXANITRODIPHENYLAMINE (HEXYL)



2,2',4,4',6,6'-Hexanitrodiphenylamine (m. p. 243-245°C) was first mentioned in the chemical literature in 1876 and as long ago as 1891 Haussermann [21] drew attention to its explosive properties. The product is known under the names of Dipicrylamine, Hexyl, Heksyl, Hexamite, Hexamin, etc.

The application of hexyl as an explosive goes back as far as 1910. It was widely used in Germany during the two World Wars, mostly in fusible compositions, with TNT and with or without ammonium nitrate as a third constituent for filling torpedoes, marine mines, bombs and whenever a particularly high explosive power was required. During World War II aluminium was also added to hexyl compositions (Vol. III).

Gnehm [22] prepared hexanitrodiphenylamine by the nitration of diphenylamine with nitric acid, while Mertens [23] used a mixture of anhydrous nitric acid with concentrated sulphuric acid for the purpose. This method was applied in 1910 for the commercial preparation of hexyl. Since the yields obtained were too low (some 60% of the theoretical), during World War I a method patented in 1895 by the Griesheim Works was introduced, the starting materials being chlorodinitrobenzene and aniline. The method consists in the preparation of dinitrodiphenylamine (m. p. 156-167°C) which is then nitrated in two stages, to obtain first tetranitrodiphenylamine (m. p. 199°C) and then hexyl:



PHYSICAL PROPERTIES

2,2',4,4',6,6'-Hexanitrodiphenylamine forms yellow needles, which decompose while melting. It is difficult to dissolve in concentrated sulphuric acid and in most organic solvents. It dissolves more easily in hot acetic acid, nitrobenzene and acetone. The pyridine salt of hexyl is still more readily soluble in acetone.

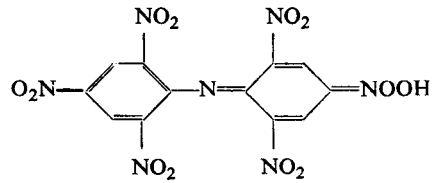
At room temperature hexyl is only slightly hygroscopic: when exposed to the air saturated with water vapour it absorbs only 0.09% moisture. The specific gravity of hexyl crystals is 1.653. Hexyl is rather difficult to press, but when mixed with 1% stearic acid more satisfactory pressing can be achieved and a uniform material obtained.

Densities obtainable under various pressures are :

below	330	kg/cm^2	density	1.43	g/cm^3
,,	660	,,	,,	1.56	,,
,,	1000	,,	,,	1.59	,,
,,	1330	,,	,,	1.60	,,

CHEMICAL PROPERTIES

The acidic character of hexyl is one of its most important features. It was first observed by Aleksandrov [24] when preparing ammonium salt of hexyl. Later this property was investigated by Hantzsch and Opolski [25], who obtained the O-methyl ether of the aci-form of hexyl, according to Hantzsch's nomenclature (Ia). The aci-form of the compound can yield salts and O-ethers (esters). It is intensely coloured due to the presence of the quinonoid ring.



Ia

The ammonium salt of hexyl known as "Aurantia" had been used for a long time as a yellow dye for silk and wool.

Hexyl seriously attacks the skin. First it dyes it yellow, then a serious eczema appears, with blisters often reminiscent of those caused by burns. Air-borne dust of the product may cause severe irritation of the mucous membranes and of the respiratory tract. Workers exposed to the action of large quantities of hexyl should be protected from inhaling its dust and from contact of the latter with the skin, by good ventilation and protective masks and clothing. The toxicity of hexyl is much higher than that of TNT (p. 161).

EXPLOSIVE PROPERTIES

Hexyl is a chemically stable compound. As van Duin and van Lennep [26] found it can withstand 30 days' heating at 95°C. They also determined its initiation temperature as being 250°C when heated at a rate of 5°/min.

Its sensitivity to impact is lower then that of tetryl but somewhat higher than that of picric acid. Kast [27] found that picric acid is exploded by a 2 kg weight falling from 60 cm, while tetryl and hexyl are exploded by fall from 40 cm.

With a 10 kg falling weight picric acid exploded at the 20 cm height, hexyl at 10 cm and tetryl at 8 cm.

Salts of hexyl, in particular those formed with heavy metals, are more sensitive to impact and friction than hexyl itself. They are inflammable and can be ignited by a flame. The ammonium salt is an exception here, being the least sensitive and not ignited by the flame, behaving like hexyl itself.

Haussermann [22] pointed out that hexyl is a more powerful explosive than TNT. Further investigations yielded the following data on the explosive properties of the substance (Kast [27]):

heat of explosion	1035 kcal/kg
volume of gases, V_0	675 l./kg
temperature, t	3450°C
specific pressure, f	9545 m

According to Kast, the heat of formation is negative and amounts to -4.6 kcal/kg (dH_f = +4.6 kcal/kg).

For rate of detonation the following figures have been reported:

at a density of 1.58 g/cm^3 6900 m/sec (J. Marshall [28])
,, ,, ,, ,, 1.64 ,, 7100 ,, (Kast [27])
,, ,, ,, ,, 1.67 ,, 7150 ,, (J. Marshall [28])

The lead block expansion given by hexyl is 325-350 cm^3 - larger than that caused by picric acid.

Hexyl can be brought to detonation as easily as tetryl, or even more easily. For example, J. Marshall [28] has determined the minimum quantities of fulminate of mercury and potassium chlorate mixtures (90:10), required for detonation of:

hexyl	0.18 g
tetry1	0.20 ,,
TNT	0.25 ,,

HEXYL MANUFACTURE

Preparation of dinitrodiphenylamine (Ludwigshafen Process)

An emulsion of 380 kg of aniline in about 1600 1. of an aqueous solution containing 230kg of sodium carbonate and 1 kg of Nekal (emulsifier) is prepared. After the emulsion has been heated to 60°C, 800 kg of molten 2,4-chlorodinitrobenzene is run in. Then the whole is heated to 90°C. The formation of solid dinitrodiphenylamine may serve as a control indicating the progress of the reaction.

The solution is cooled to about 50°C, dinitrodiphenylamine is separated by tentrifuging, washed with diluted acid (from the nitration process) to remove aniline, then thoroughly with water, dried at 100°C and pulverized. The product can be obtained in almost theoretical yield 95-98%.

Nitration of di- to tetra-nitrodiphenylamine (after J. Marshall [28])

100 parts of dry dinitrodiphenylamine are charged into the nitrator, containing 350-400 parts of a nitrating mixture of the composition:

HNO_3	30-45%
H_2SO_4	40-50%
H_2O	15-20%

a temperature of 70°C being maintained during this procedure. When all the substance has been run in, the whole is heated to 80-90°C and kept at this temperature until nitrogen dioxide stops evolving, which takes about 2 hr. Then the nitrator contents are cooled and the yellowish brown crude product is separated from the spent acid by filtration.

The approximate composition of the spent acid obtained in a series of runs averaged :

HNO_3	14%
H_2SO_4	51%
nitrosylsulphuric acid	7.5%
H_2O	26%
organic matter	1%

Nitration of tetranitrodiphenylatiine to hexyl (after J. Marshall [28]).

Immediately after being filtered off, tetranitrodiphenylamine (containing some acid) is taken in a quantity corresponding to 100 parts of the dry substance and added to 375 parts of a nitrating mixture:

HNO_3	60%
H_2SO_4	40%

When using a mixture poorer in nitric acid, consisting e.g. of 25% of HNO_3 and 75% of H_2SO_4, a very fine crystalline product difficult to filter is obtained.

During the reaction a temperature of 70°C is maintained. After all the tetranitrodiphenylamine has been added, the reaction mixture is heated to 90°C, kept at this temperature for one hour, cooled down to room temperature and filtered on a vacuum filter. A yellow crystalline, easily filterable product is obtained. The spent acid is approximately of the following composition:

HNO_3	34%
H_2SO_4	40%
nitrosylsulphuric acid	11%
organic matter	1%

The product is well washed with water, then transferred to a washing tank, where it is washed 2-3 times by agitating with boiling water. The washings are separated by decantation. The water remaining in the washed product is separated on a vacuum filter (J. Marshall recommends a centrifuge for this purpose but this procedure should be considered as too hazardous). The wet product, after being dried at 80°C, is of high purity, as reflected by its melting point which ranges from 238.5° to 239.5°C.

The yield obtained for the conversion of dinitrodiphenylamine into hexyl is 86% of the theoretical.

Japanese method

Japanese process for preparing hexanitrodiphenylamine from dinitrodiphenylamine was applied at the Maizuru Works. A stainless steel nitrator is charged with 80% nitric acid, followed by dinitrodiphenylamine. A temperature of 45-55°C is maintained during this procedure, which takes 4 hr. Then the temperature is raised to 90-95°C during one hour and a half and kept there for another hour and a half. Then the whole is cooled to 45°C, the precipitated hexanitrodiphenylamine is filtered off on a vacuum filter and transferred to a tank, where it is washed with cold water, then three times with hot water, and finally again with cold water. The remaining water is separated from hexyl by centrifugation, followed by drying.

The spent nitric acid may be fortsed by mixing with 98% nitric acid.

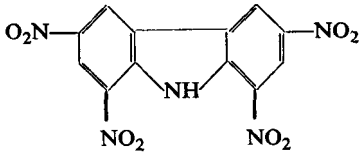
NITRO DERIVATIVES OF CARBAZOLE

The nitration of carbazole has been studied by Graebe [29], Ciamician and Silber [30], VotoEek [31], Escales [32] and Raudmtz [33].

Mono-, di- and tetra-nitro derivatives of carbazole have been obtained. Among them only tetranitrocarbazole is of practical importance. It was used in Germany under the name of “Nitrosan” as an insecticide. During World War II it was used under the name of “Gelbmehl” in combustible compositions for delayed action time fuses.

TETRANITROCARBAZOLE

There are two isomeric tetranitrocarbazoles: 1,3,6,8- (I) (m.p. 296°C) and 1,2,6,8- (II) (m.p. 153-154°C).



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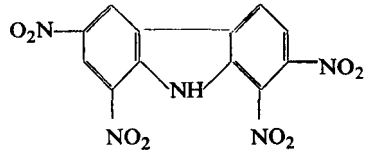
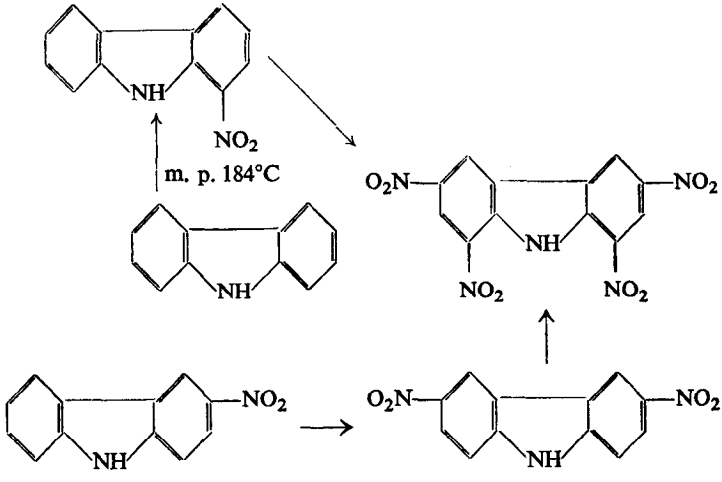


I-I

They are usually prepared by the direct nitration of carbazole with a mixture of nitric and sulphuric (or acetic) acid. The most convenient way of nitrating carbazole is sulphonation followed by the action of concentrated nitric acid. 1,3,6,8-Tetranitrocarbazole (I) is obtained as the principal product.

The following intermediate products have been isolated in the course of the nitration of carbazole :

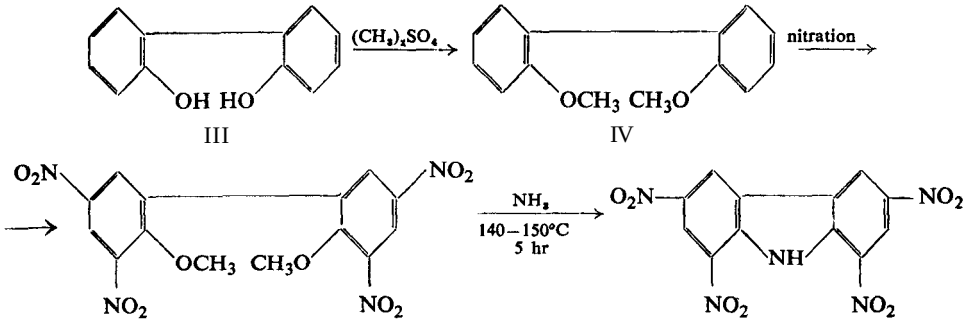


m. p. 210°C m. p. 320°C

In addition to the 1,3,6,8-isomer a product, named by Ciamician and Silber the γ– isomer, has been obtained, which, according to recent investigations, has proved to be the 1,2,6,8-isomer (II). From the reaction product pure compound I may be isolated by extraction with toluene, followed by crystallization from acetic acid. The pure product I may also be obtained by treating the crude product with sodium sulphite. According to Murphy, Schwartz, Picard and Kaufman [34], the melting point of the product may be raised in this way from 278° to 296°C at the cost of a 10% loss of yield. The same authors found that during the nitration process the 1,2,6,8-isomer (II) is formed along with the principal product. This isomer may be obtained in a larger quantity if carbzole is subjected to sulphonation with oleum prior to nitration.

The constitution of tetranitrocarbazole (I) was determined by Borsche and Scholten [35] from the following reactions, of which the final stage was the formation

of tetranitrocarbazole with a certain quantity of 3,3',5,5'-tetranitro-2,2'-dimethoxydiphenyl (V). The sequence of the reactions was as follows:



(3)

MANUFACTURE OF 1,3,6,8-TETRANITROCARBAZOLE

In a method applied at Höchst, 1896 kg of 96% sulphuric acid are charged into the sulphonator, followed by 950 kg of commercial grade carbazole (88-95° purity). The whole is stirred at room temperature for 50 min. Then the temperature is raised to 95°C and stirring is continued until a sample taken from the sulphonator dissolves completely in water. At this stage of the process disulphonic acid is formed. Then the sulphonator contents are cooled to 70°C and the remainder of the sulphuric acid, i.e. 1561 kg (the total quantity being 3430 kg) is added. Further sulphonation takes place, resulting in the formation of 1,3,6-trisulphonic acid.

It has been proved that carrying out the reaction in two stages, as described above, makes the sulphonation process proceed more quietly and prevents the SO_3H group from entering position 7 (otherwise, the sulpho group in position 7 would not be substituted by a nitro group, causing the nitration product to remain soluble in water).

A two stage process is applied for the nitration of the sulphonic acid obtained. The product is transferred to nitrator I and here half the total nitrating acid is added. Then half the contents of nitrator I are transferred to nitrator II followed by the second half of the nitrating acid. The sulphonated product is transferred from the sulphonator to nitrator I, containing half of the previous batch, for repeating the first nitration stage, then half of this reaction mixture is transferred to nitrator II, and so on.

Nitrator I contains half of the previous batch to which the sulphonator contents and a portion of nitrating acid, consisting of 870 kg of concentrated nitric acid and 4350 kg of 20% oleum, have been added. The nitrating acid should be run into the nitrator at a temperature of 40°C (vigorous cooling is necessary). This nitration stage, including the transfer of the sulphonated product, takes about 8 hr.

The other half of the contents of nitrator I is conveyed to nitrator II and the second half of the nitrating mixture, consisting of 870 kg of concentrated nitric acid and 4350 kg of 20% oleum, is run in, a temperature of 50°C being maintained.

Then the whole is heated to 60°C which initiates a further spontaneous temperature rise. Care should be taken by cooling to prevent the temperature rising above 95°C, otherwise the yield might decrease. The process in nitrator 11, including the transfer of contents from nitrator I, takes approximately 8 hours.

Half the contents of nitrator II is then transferred to a tank with 6000 1. of water, a temperature of it below 50°C being maintained. This operation requires from 4 to 6 hr, and when the tank has been discharged, the second half of the contents of nitrator I1 is treated in the same way.

The precipitated product is filtered off and washed with water warmed to a temperature not exceeding 50°C. Since moist tetranitrocarbazole is thixotropic the filtration and washing is rather difficult to effect. The moist product is mixed in a tank with a concentrated solution of 20 kg of sodium carbonate to deacidify it, then filtered off and dried.

The product meets the following specifications:

melting point	281-290°C
sulphur content	0.8-1.3%
moisture	1-2%
nitrogen content	18.5-19.5% (theoretical 20.2%)

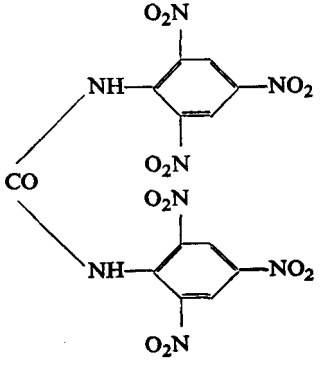
PREPARATION OF 1,2,6,8-TETRANITROCARBAZOLE

According to Murphy, Schwartz, Picard and Kaufman [34], 50 parts of carbazole is dissolved in 300 parts of 30% oleum at a temperature of 40-50°C. The mixture is kept at 90-100°C for 2 hr. A sample of the mixture taken after this time should dissolve completely in water. Then the mixture is cooled and 160 parts of 93% nitric acid are added, the temperature being maintained at 40-60°C. 1,2,6,8-Tetranitrocarbazole precipitates, and may be recrystallized from nitrobenzene solution. The 1,3,6,8-isomer remains in the solution.

AMIDE DERIVATIVES OF TRINITROANILINES

Several rather simple acid amides have been tested as explosives. However, they have not found practical used since they readily undergo hydrolysis.

HEXANITRODIPHENYLUREA



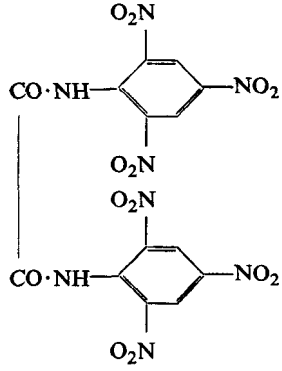
Hcxanitrodiphenylurea (hexanitrocarbanilide, sym-dipicrylurea) forms pale yellow crystals melting at 208-209°C (with decomposition). It was obtained by Perkin [36] and Reudler [37]. Davis [38] was the first to suggest its use as an explosive. The compound is prepared by the nitration of sym-diphenylurea, which may be obtained by reacting phosgene with aniline, or more simply, by heating aniline with urea at 160-165°C. Davis proposed the nitration of diphenylurea in two stages: first tetranitrodiphenylurea is obtained, and this in turn is nitrated to hexanitrodiphenylurea.

When heated with dilute sulphuric acid, hexanitrodiphenylurea is hydrolysed, forming picric acid. With ammonia it produces a deep red colour, which is ascribed to the formation of an ammonium salt of the aci-form. Boiling with aqueous ammonia solution causes hydrolysis with the formation of picramide.

The compound has a high initiation temperature (345°C). However, because of its susceptibility to hydrolysis its chemical stability is too low for it to be used as an explosive, although its explosive power is somewhat higher than that of TNT. Its sensitivity to impact is similar to that of tetryl.

HEXANITRO-OXANILIDE

The use of hexanitro-oxanilide (m. p. 295-300°C) as an explosive material was suggested by the Societe Anonyme d'Explosifs [39].

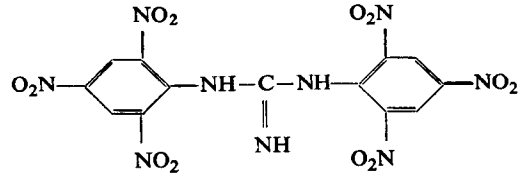


The compound is prepared by the direct nitration of oxanilide (Mixter and Walther [40]). Domanski and Mieszkis [41] investigated the explosive properties of hexanitro-oxanilide and found the following values for the rate of detonation of the pressed product mixed with 2% of dinitrotoluene:

at a density of	0.90	g/cm^3	5100 m/sec
„ „ „ „	1.20	„	5500 „
„ „ „ „	1.47	„	6800 „

It follows from the above that the explosive power of the compound is similar to that of TNT. The fact that it readily undergoes hydrolysis, forming picric acid and oxamide is a serious drawback and prevents its use as au explosive.

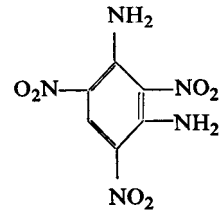
HEXANITRODIPHENYLGUANIDINE



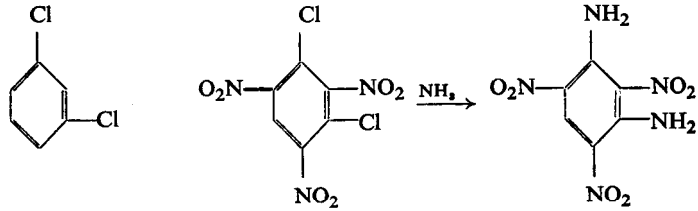
This compound was suggested by Jackman and Olsen [42] as an explosive. The authors prepared it by the nitration of diphenylguanidine.

NITRO DERIVATIVES OF AMINOPHENOLS

TRINITRO-m-PHENYLENEDIAMINE



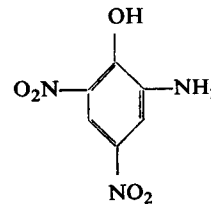
This explosive (m. p. 285°C) was first obtained by Korner and Contardi [43] in 1909, using the reaction:



The compound may also be prepared by other methods; for example, van Duin and van Lennep [26] obtained it by reacting ammonia with trinitroanisidine. They also investigated its explosive properties.

The compound is known to be stable : when heated at 95°C for 30 days it remains unchanged. However, on boiling with a dilute sodium hydroxide solution it decomposes to trinitroresorcinol and ammonia. It is less sensitive to impact than tetryl, but more sensitive than picric acid. The initiation temperature is 335°C.

PICRAMIC ACID

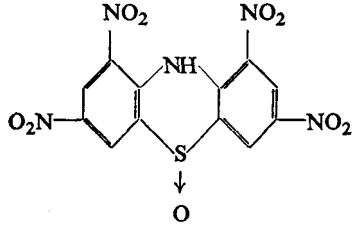


Picramic acid or 4,6-dinitro-2-aminophenol (m. p. 169-179°C) forms dark red crystals, readily soluble in benzene and acetic acid, but difficult to dissolve in other organic solvents.

The compound is prepared by reacting sodium sulphide with picric acid (Girard [44]). It is of some importance as an intermediate in the manufacture of azo dyes. It has not found any use as an explosive. being none the less a source for the initiating explosive dinitrodiazophenol (Vol. III).

NITRO DERIVATIVES OF PHENOTHIAZINE

Phenothiazine nitrated to its tetranitro derivative was used by the Germans during World War II as a component of a non-fusible explosive composition known under the name of "Pressling". Monard, Ficheroulle and Fournier [45] found the compound to be phenothiazine tetranitrosulphoxide (I) (m. p. 368°C):



The compound may be prepared in 70% yield by the nitration of phenothiazine with a mixture of 98% nitric acid and anhydrous sulphuric acid at 60°C. In addition to nitration, oxidation of the sulphur atom also takes place, resulting in the formation of the sulphoxide.

Bernthsen [46], Kehrmann and co-workers [47] and Gilman and Shirley [48] also observed similar oxidation of the sulphur atom when nitrating phenothiazine derivatives. The oxidation of sulphur to the sulphonyl group has been observed in the nitration of diphenyl sulphide (p. 554). As T. Urbanski, Szyc-Lewatiska and Kalinowski [49] found, methylene blue, when nitrated, yields derivatives having a sulphonyl group (see Vol. III for more details).

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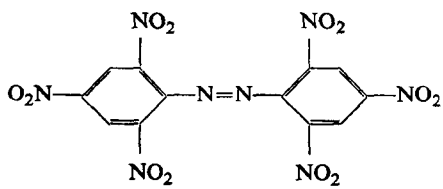
CHAPTER XVIII

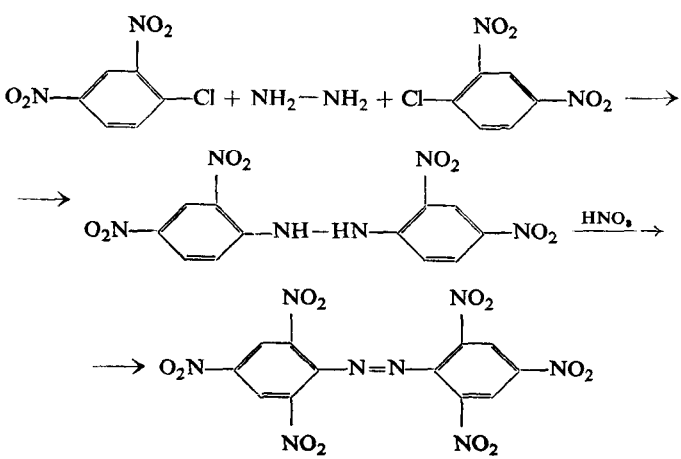
NITRO DERIVATIVES OF AZO- AND HYDRAZO-BENZENES

NITRATION of azo compounds leads to mixtures of nitro derivatives of azo and azoxy compounds (Werner and Stiasny [l]). Thus, by nitrating azobenzene with 98% nitric acid at a temperature not exceeding +6°C, these authors obtained a mixture of *p*- nitroazobenzene, *p,p'*- dinitroazobenzene and *p*- nitroazoxybenzene. With 98% nitric acid without cooling, mainly a mixture of the trinitroazoxybenzene isomers was obtained.

HEXANITROAZOBENZENE



2,2',4,4',6,6'-Hexanitroazobenzene (m. p. 215-216°C) forms orange coloured needles. It was prepared by Grandmougin and Leeman [2] by acting with hydrazine on picryl chloride. In a more recent method chlorodinitrobenzene is reacted with hydrazine to yield tetranitrohydrazobenzene which is then further nitrated. Simultaneously the oxidation of the hydrazo to an azo group takes place:

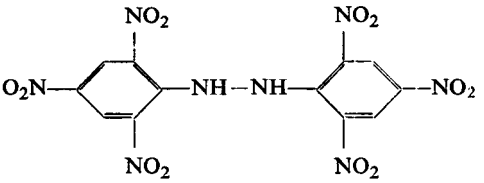


(1)

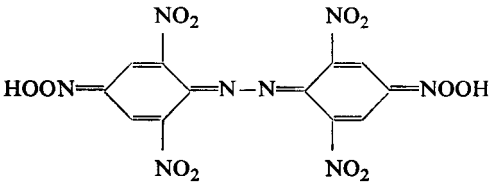
The process is carried out in water suspension in the presence of agents to bind the hydrogen chloride evolved.

Hexanitroazobenzene is a more powerful explosive than hexyl, being of the same order as tetryl. Sensitivity to impact is also similar to that of tetryl.

HEXANITROHYDRAZOBENZENE



The compound (m. p. 210-202°C) was first obtained by Grandmougin and Leeman [2] in 1908. They reacted picryl chloride with hydrazine. The product is rather reactive: for example, its aci-form



readily forms salts with metals. It can also be oxidized to hexanitroazobenzene and in the presence of aniline internal oxidation to a phenazine compound takes place. That is why it has not been regarded as an explosive of any practical value.

The same holds for pentanitrohydrazobenzene $C_6H_3(NO_2)_2NH\text{-}NHC_6H_2(NO_2)_3$, which may be obtained by reacting picryl chloride with dinitrophenylhydrazine.

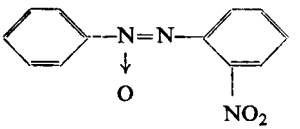
NITRO DERIVATIVES OF AZOXYBENZENE

Nitration of azoxybenzene may lead to the formation of various nitro derivatives, differing in the number of nitro groups.

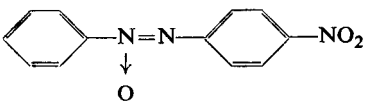
MONONITRO DERIVATIVES

Thus, when nitrated with nitric acid alone (sp. gr. 1.45) azoxybenzene yields a mixture of 2- and 4-nitroazoxybenzenes (I) and (II) (Zinin [3] ; Werner and Stiasny [1]).

The 4-isomer has two crystalline forms IIa and IIb (Angeli and Alessandri [4]; Angeli and Valori [5]).



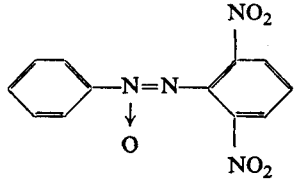
I
m. p. 49°C



II
m. p. 153°C (IIa)
149°C (IIb)

DINITRO DERIVATIVES

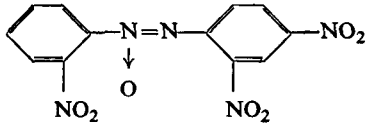
More vigorous nitration with nitric acid of specific gravity 1.48 and at temperatures up to 100°C results in the formation of 2,6-dinitroazoxybenzene (III) (Valori [6]).



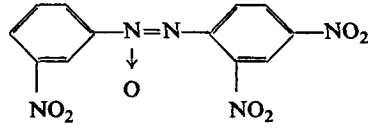
III
m. p. 172°C

TRINITRO DERIVATIVES

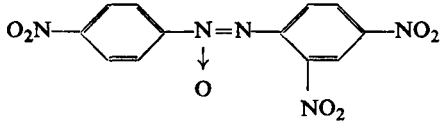
Even more vigorous nitration, with boiling nitric acid of specific gravity 1.51, leads to the formation of a mixture of trinitroazoxybenzenes: 2,4,2'- (IV); 2,4,3'- (V) and 2,4,4'- (VI):



IV
m. p. 192°C



V
m. p. 178°C



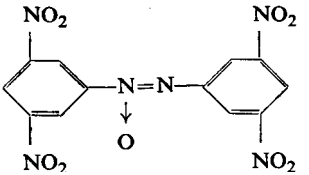
VI
m. p. 135-136°C

All the compounds are formed in the nitration of azobenzene (Werner and Stiasny [1]).

The 2,4,4'-isomer may also be obtained either by the nitration of azobenzene or of 4,4'-dinitroazoxybenzene with nitric acid sp. gr. 1.51 Klinger and Zuurdeeg [7]). 4,4'-Dinitroazoxybenzene may be obtained by the action of alkalis on *p*- dinitrobenzene (Lobry de Bruyn [8]; Lobry de Bruyn and Blanksma [9]; Lobry de Bruyn and Greuns [10]) or by the oxidation of *p*- nitroaniline with persulphuric acid (Bamberger and Hübner [11]).

TETRANITRO DERIVATIVES

To obtain higher nitrated azoxybenzenes, indirect nitration methods must be applied. 3,5,3',5'-Tetranitroazoxybenzene (VII), for example, may be prepared from sym-trinitrobenzene either by boiling with a dilute sodium carbonate solution (Lobry de Bruyn and Leent [12]) or by partial reduction (Blanksma [13]).

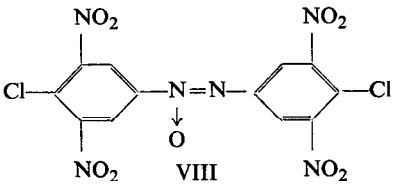


VII

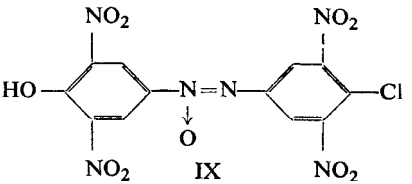
m. p. 185°C

It is interesting to note that the two azoxybenzene rings differ in their readiness to be nitrated. Angeli [14] was the first to draw attention to this fact. From it he inferred that the azoxy group has an unsymmetrical structure: -N=N-. This
↓
O
opinion was confirmed later by several authors (e.g. G. M. Robinson [15] ; Behr [16]; T. Urbanski and J. Urbanski [17]).

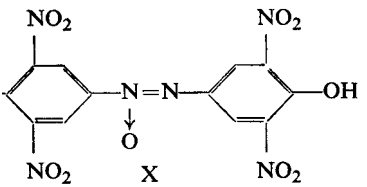
Among other higher nitrated azoxybenzene derivatives the following chloro-, phenol-, methoxy- and methylamine derivatives were recently obtained by T. Urbanski and J. Urbanski [17] :



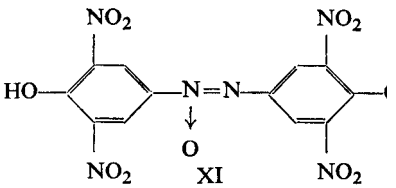
m. p. 226-228°C



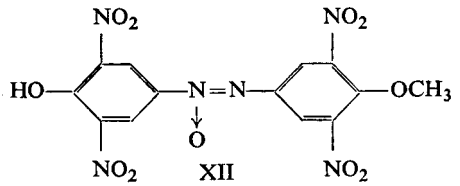
m. p. 198-201°C



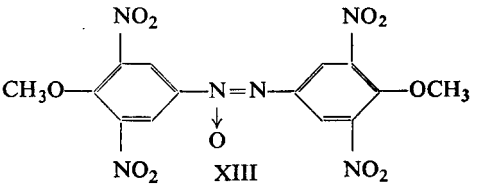
m. p. 214-217°C



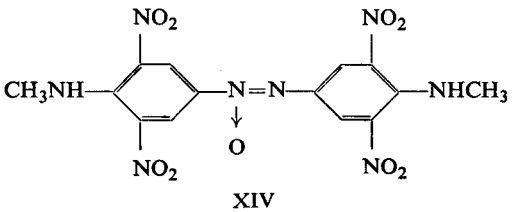
m. p. 186487°C



m. p. 191-192°C



m. p. 239-240°C



XIV

m. p. 260-261°C (decomposition)

The successful preparation of isomers IX and X as well as the different reactivities of the chlorine atoms in the two rings of compound VIII and different tendency to hydrolysis shown by the methoxy groups in compound XIII provide further evidence in favour of an unsymmetrical structure of the azoxy group, in accordance with Angeli's view.

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CHAPTER XIX

ALIPHATIC NITRO COMPOUNDS

UNTIL recently only the higher nitrated paraffins were considered to have explosive properties or to be of use in explosive compositions. It was only quite recently that nitromethane was discovered to possess powerful explosive properties, although it requires a strong initiator. Among other nitro compounds tetranitromethane deserves special attention. Due to its high oxygen content it may be considered as an oxygen carrier.

NITROMETHANE

Nitromethane, CH_3NO_2, is a volatile liquid. It may be obtained by direct vapour phase nitration of paraffinic hydrocarbons either with nitric acid vapours (Hass et *al.* [l-8]) or with nitrogen dioxide (T. Urbanski and Slebodzinski [9]). It may also be prepared by the action of sodium- or potassium nitrite on chloroacetic acid (Kolbe [10]):

$$NaNO_2 + ClCH_2COOH \rightarrow NaCl + CH_3NO_2 + CO_2 \quad (1)$$

or by reacting dimethyl- or methylsodium sulphate with sodium nitrite (Krause Elm:

$$2NaNO_2 + (CH_3)_2SO_4 \rightarrow 2CH_3NO_2 + Na_2SO_4 \quad (2)$$

$$NaNO_2 + CH_3NaSO_4 \rightarrow CH_3NO_2 + Na_2SO_4 \quad (2a)$$

A method consisting in reacting silver nitrite with methyl iodide or bromide is of value as a laboratory method only.

In 1951 Médard [12] found that nitromethane could be detonated by means of a strong initiator.

As a combustible with a rather high oxygen content nitromethane, alone or in various mixtures, has been gaining even increasing use as a rocket fuel. This great interest in nitromethane provided an incentive for the investigation of its physical and chemical properties.

PHYSICAL PROPERTIES

According to Toops [13], the boiling point of nitromethane at 760 mm is 101.2°C and the temperature coefficient of pressure dp/dt is 0.0427°/mm, its freezing point is -28.55°C and its density at 20° and 30° is 1.13816 g/cm^3 and 1.12439 g/cm^3 respectively.

The temperature coefficient of density dd/dt = 0.001377.

A number of authors have determined vapour pressures of nitromethane (Hodge [14]; W. M. Jones and Giauque [15]). More recent data are given by McCullogh, Scott *et al.* [16]:

Temperature, °C	55.71	61.30	72.56	83.92	95.41	101.19	112.83	124.56	136.40
Vapour pressure, mm Hg	149.4	187.6	289.1	433.6	634.0	760.0	1074.6	1486.1	2026.0

Vapour pressure can be expressed by the Antoine equation:

$$\log p = 7.274170 - 1441.610 / (t + 226.939) \tag{3}$$

Cox [17] suggested another equation:

$$\log P = A\,(1 - 374.347 / T) \tag{4}$$

Here $\log A = 0.845118 - 6.1497 \times 10^{-4}T + 6.0541 \times 10^{-7}T^2$, p is in mm Hg, P in atm, t in °C, T in °K.

McCullogh, Scott et al. [16] pointed out that Cox's equation also holds true beyond the usual experimental temperature range: 55 - 136°C.

Pitzer and Gwinn [18] and later McCullogh, Scott et al. [16] determined the heat of vaporization of nitromethane:

at 45.3°C ΔH_v = 8883±l cal/mole
at 101.4°C ΔH_v = 8120±1 cal/mole

The following empirical equation has been given by McCullogh and his colleagues :

$$H_v = 11730 - 4.9977\ T - 1.24 \times 10^{-2}T^2 \text{ cal/mole} \tag{5}$$

The heat capacity of the vapour is given approximately by eqn. (6):

$$C_p = C_p^0 - PT\left(\frac{d^2B}{dT^2}\right) + 2[P^2/R]\left[B\left(\frac{d^2B}{dT^2}\right)\right]\left[1 - 3\frac{BP}{RT}\right] \tag{6}$$

C_p^0 is the heat capacity in the ideal gaseous state and B is the second virial coefficient. The last term in eqn. (6) is usually neglected, but for a highly polar molecule, such as that of nitromethane, it should be retained.

C_p^0 and B are given by the following equations:

$$C_p^0 = 2.352 + 4.288822 \times 10^{-2}T - 1.694 \times 10^{-5}T^2 \text{ cal deg}^{-1} \text{ mole}^{-1} \tag{7}$$

$$B = -300\text{-}12.97 \exp (1700/T) \text{ cm}^3 \text{ mole}^{-1} \tag{8}$$

McCullogh, Scott et al. also give the values of thermodynamic functions such as entropy, standard heat, standard free energy etc., at temperatures from 0° to 1500°K.

The heat of combustion of nitromethane at atmospheric pressure and 20°C is 169.4 kcal/mole, according to Kharasch [19].

The standard heat of formation of liquid nitromethane H_f^0 (liq.) is -27.03± 0.15 kcal/mole at 298.16°K.

The standard heat of formation in the gaseous state ΔH_f^0 (gas.) is -17.86 kcal/mole at 298.16°K (McCullogh, Scott et al. [16]).

The other physical constants are:

Viscosity at 15°C 0.694 cP
at 30°C 0.595
(according to Tikmermans and Hennalt-Roland [20])
Surface tension at 15°C 37.74 dynes/cm
at 30°C 35.48
(according to Hennaut-Roland and Lek [21]).

STABILITY

When stored in glass apparatus at a temperature slightly higher than room temperature (30°C) nitromethane was found to develop a partial vacuum (0.2 atm) (Bellinger, Friedmann, Bauer, Eastes, Bull [22]). This indicates an absorption of oxygen insufficient, however, to change the appearance or other physical properties of the substance. On long storage at 48.9°C or more, nitromethane undergoes slight decomposition with the evolution of traces of nitrogen dioxide.

The thermal stability of nitromethane can be improved by adding a small amount of boric acid. It reduces the tendency of nitromethane to decompose on distillation (Lippincott [23]). The addition of a small amount (0.2-1.0%) of phenolic antioxidants, such as hydroquinone, has also been suggested, i.e. substances having a critical oxidation potential as low as the air oxidation potential of α– naphthol (Senkus [24]).

IGNITION AND BURNING

Nitromethane can be ignited by an open flame. Corelli [25] reported, that the "flash point" in the Abel-Pensky apparatus is 35-37°C and the temperature of auto-ignition is 440°C (Constam and Schlaepfer's method).

The flash point (by Marcusson's method) is 42-43°C. Makovky and Lenji [26] report that nitromethane has a threshold explosion temperature of 312°C.

The problem of ignition is very important when nitromethane is to be used as rocket monofuel. Ignition of nitromethane with oxygen is not reliable (Bellinger, Friedmann, Bauer, Eastes, Goss [22]) and very often leads to ignition failure and explosion. The presence of oxygen makes nitromethane more sensitive to detonation.

There is very little danger that burning nitromethane will explode. The following test, described by Commercial Solvents Corporation [27], is rather significant from this point of view. A 55-gallon sealed drum filled with nitromethane, was enclosed in a concrete chamber in a mass of pine wood which was ignited quickly throughout by charges of smokeless powder. Although the temperature inside the chamber was higher than 700°C the heat merely caused the drum to burst, after which the contents burned quietly for about 30 min.

Since nitromethane should be considered as an oxidizing agent and since at elevated temperatures the oxidation processes can assume a rapid rate, it is recommended that nitromethane should not be heated in the presence of hydrocarbons or other combustible substances in a confined space. Thus explosion may occur during the heating of nitromethane-lubricating oil mixtures to high temperature under pressure.

The possible use of nitromethane as a liquid monofuel for rocket propulsion has aroused interest in the problem of its thermal decomposition.

Although this has come about only recently, the first experiments on the subject were carried out as long ago as 1935 by H. A. Taylor and Vesselovsky [28]. The experiments were related to the temperature range of 380-420°C and 200 mm pressure. The reaction was found to be of the first order, with an activation energy of 61.0 kcal/mole.

Subsequently, Frejacques [29] and Cottreh, Graham and Reid [30] continued the experiments within the ranges of 310-440°C and 380-430°C, under 4-40 mm and 200-400 mm pressures respectively. They confirmed the previous statement that the reaction is of the first order, with activation energies of 42.8 and 53.6 kcal/mole respectively. The reaction constant, ***k,*** may be calculated, according to Cottrell et ***al.,*** from the equation

$$k = 10^{14.6} \exp \frac{-53{,}600}{TR} \text{ sec}^{-1} \qquad (9)$$

Hillenbrand and Kilpatrick [31] investigated the same problem at 420-480°C. They confirmed the previous results and obtained a value of 50,000 for the activation energy.

Gray, Yoffe and Roselaar [32] examined the decomposition of nitromethane at 447°C.

Experiments by Müller [33] and Makovky and Günwald [34] on the decomposition of nitromethane under pressures of 12.2-20.2 and 40 atm and at temperatures of 355°C and 312-340°C respectively are particularly interesting. The reaction constant, according to these investigators, was

$$k = 5.4 \times 10^{13} \exp \frac{-49{,}200}{R_T} \text{ sec}^{-1} \qquad (10)$$

T. Urbanski and Pawelec [351 found the activation energy to be 45.0 kcal/mole for the range 460-570°C.

The products of decomposition at low pressures were: NO, N_2O. H_2O, CO, CO_2, CH_4, small amounts of ethylene and ethane, and trace of NO_2 (Cottrell ef al. [30]). Nitrogen oxide was the principal nitrogen-containing compound.

Decomposition under pressure led to the formation of N_2, NO, H_2O, CO, CO_2, CH_4, HCN and small quantities of CH_3CN, C_2H_5CN, CH_2O, N_2O (Müller [33]).

The main difference between decomposition at high pressure and at low pressure is the presence of hydrogen cyanide as the principal carbon compound in the former case.

In addition to gaseous products, solid (ill-defined) compounds formed, particularly when decomposition took place at high pressure.

The presence of oxygen accelerated decomposition, whereas hydrogen slowed it down. Addition of small amounts of nitrogen oxide or nitrogen dioxide had no influence on the rate of decomposition under high pressure, although high concentrations of these-gases had an inhibiting effect.

With regard to the mechanism of decomposition, some authors (Taylor and Vesselovsky [28]) suggest N-O bond fission

$$CH_3NO_2 \rightarrow CH_3NO + O \tag{11}$$

while others (Frkjacques [29], Cottrell et al. [25], Gray et al. [32]) assume the rupture of C-N bond:

$$CH_3NO_2 \rightarrow CH_3 + NO_2 \tag{12}$$

More recently Müller, and also Makovky have reported both mechanisms taking place at elevated pressure.

Hillenbrand and Kilpatrick [31] suggested that the decomposition was partly due to intramolecular rearrangement. Makovky assumes that it proceeds by a radical chain mechanism with very short chains.

The following scheme has been suggested by Taylor and Vesselovsky [28] for the initial steps of the reaction at low pressure:

$$CH_3NO_2 \rightarrow CH_3 + NO_2 \tag{13a}$$

$$CH_3 + CH_3NO_2 \rightarrow CH_4 + CH_2NO_2 \tag{13b}$$

$$CH_2NO_2 + NO_2 \rightarrow CH_2O + NO + NO_2 \tag{13c}$$

$$CH_2O + NO_2 \rightarrow CO + NO + H_2O \tag{13d}$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \tag{13e}$$

At high pressure the following radical reactions also take place:

$$CH_3NO_2 \rightarrow CH_3NO + O \tag{14a}$$

$$O + CH_3NO_2 \rightarrow CH_2O + HNO_2 \tag{14b}$$

$$CH_3 + CH_3NO_2 \rightarrow CH_4 + CH_2NO_2 \tag{14c}$$

It is possible that the presence of hydrocyanic acid in the product of decomposition at high pressure may be ascribed to the formation of CH_3NO:

$$CH_3NO + CH_2{=}NOH \rightarrow HCN + H_2O \quad (15)$$

(reaction described by Mitchell and Hinshelwood [36]).

Nitrosomethane is likely to be formed as a result of N-O fission or from the CH_3 radical :

$$CH_3 + NO \rightarrow CH_3NO \quad (16)$$

EXPLOSIVE PROPERTIES

Reliable evidence that nitromethane possesses properties characteristic of an explosive has been provided relatively recently. In particular two disastrous railway accidents which occurred in 1958 in the U.S.A. (one at Niagara Junction and the other at Mount Pulaski, Ill.) gave decisive proof that nitromethane should be considered as an explosive and classified as such when subjected to transportation. Both accidents occurred with nitromethane in tank cars. Since then nitromethane has been the only nitroparaffin which is not allowed to be shipped in tank cars but only in smaller containers, such as drums.

Bellinger, Friedmann, Bauer, Eastes and Bull [22] brought about the detonation of nitromethane confined in a heavy-walled container by the severe impact produced by firing 0.50 caliber ammunition at it. When a thin-walled container was substituted for the heavy-walled one, no detonation occurred. According to Cass [37], nitromethane subjected to an impact test exploded under the impact of a 2 kg weight falling from a height greater than 1.95 m. Nitroglycerine explodes under similar conditions when the dropping height is only 35 cm. According to Commercial Solvents Corporation [27], liquid nitromethane can detonate under a sudden impact of compressed air ca. 2000 lb/in^2. Apparently air compressed to 1200 lb/in^2 may be applied safely.

Nitromethane will detonate only when a very strong initiator is used. According to Makovky and Lenji [26], 10 g of hermetically sealed nitromethane can be detonated by 2.5 g of tetryl initiated in turn by 0.5 g of lead azide.

According to T. Urbanski and Pawelec [35], nitromethane could not be detonated completely by means of a No. 8 detonating cap alone or with addition of 1-8 g of tetryl, when nitromethane was confined in copper tubes of 13.6/14.8 mm and 23/25 mm diameter and 15 cm length.

The sensitivity of nitromethane to detonation increases with increase in temperature. The following figures (Table 122) were obtained by Kaplan, Johnston, Sill, and Peebles [38]. Nitromethane was confined in 3 in. stainless-steel tubing and explosion was initiated by No. 8 detonator.

The addition of certain compounds can render nitromethane more sensitive to detonation by a No. 8 cap, for instance strong bases and acids, such as aniline, ethylenediamine, methylamine, aqueous NH_3, KOH, Na_2CO_3, formic, nitric, sulphuric and phosphoric acids.

TABLE 122

°F	°C	Number of tests	Number of explosions
60-90	15.6-32.2	numerous	0
100-110	31.8-43.3	25	1
120-125	38.9-51.7	13	4
130-140	54.4-60	10	5
160-180	71.1-82.2	18	13

The data on the rate of detonation of nitromethane have been obtained only recently.

Médard [12] found the rate to be 6600±132 m/sec when in a glass tube 30 mm in diameter and 1.8 mm thick, or in an aluminium tube of the same diameter and 2.5 mm thick. A particularly strong initiator was used. Nachmani and Manheimer [39] reported lower figures (Table 123 and 124).

TABLE 123

NITROMETHANE CONFINED IN PAPER

Diameter mm	Detonation rate m/sec
44	6280
34	6260
29	6150
26.5	partial detonation
25	no detonation

TABLE 124

NITROMETHANE CONFINED

Tubes made of:	Internal diameter mm	Wall thickness mm	Detonation rate m/sec
iron	40	4	6320
	27	3	6300
	25	17	6280
brass	7	0.8	6060
polyvinyl chloride	7.5	1.0	no detonation
rubber	8	2	,,
	10	3	,,
polyester	8	7	,,

According to T. Urbanski and Pawelec [35], the rate of detonation of nitromethane can be expressed by the following figures (Table 125).

TABLE 125

Tubes made of:	Diameter mm	Initiation	Rate of detonation average values m/sec	Method
copper	18/20	No. 8 detonator and 1-5 g tetryl	6190	Dautriche
copper	23/25			
steel	22/27			
copper	18/20	No. 8 detonator and 6.2g tetryl	6405	Electric Chronograph

Van Dolah, Herickes, Ribovich and Damon [40] found values of 6275 and 6285 m/sec in steel and aluminium tubes respectively of 27 mm internal diameter. The same authors confirmed that addition of small quantities of various substances significantly affects the susceptibility to detonation of the resulting solution.

Bases (ethylenediamine, triethylamine, pyridine) were found to be strong sensitizers. Acids (sulphuric acid, acetic acid) were found to be much weaker sensitizers. Dibutyl phthalate, benzene, cyclohexane were found to be weak desensitizers.

According to Médard [12], in the lead block test nitromethane gives figures similar to picric acid. T. Urbanski and Pawelec [35] found 325-360 cm^3, averaging 345 cm^3, i.e. 110% of that of picric acid. The same authors determined the lead block expansion when nitromethane was detonated by means of a No. 8 detonator and 1 or 5 g of tetryl. The expansion given by tetryl was deducted from the bulk expansion (Table 126).

TABLE 126

Charge			Expansion	
nitromethane 8 -	detonator No.	tetryl g	total cm^3	after deduction of tetryl expansion cm^3
10	8	1	445	420
-	8	1	25	
10	8	5	640	
-	8	5	145	495

Salts of nitromethane are extremely sensitive to flame and bum readily. They are also sensitive to friction, impact and electric discharge. Mercuric salt can be transformed into mercuric fulminate (Vol. III).

DINITROMETHANE

$CH_2(NO_2)_2$

Dinitromethane is a volatile liquid with a sharp, acid smell. It was first obtained by Villiers [41] and Losanitsch [42]:

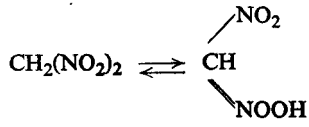
$$\begin{matrix}CH_2Br\\|\\CH_2Br\end{matrix} \xrightarrow{HNO_3} CBr_2(NO_2)_2 \xrightarrow[\text{alcoh.}]{KOH} CKBr(NO_2)_2 \xrightarrow{H_2S} CH_2(NO_2)_2 \qquad (17)$$

Duden [43] improved the last stages of the method:

$$CBr_2(NO_2)_2 \xrightarrow{KOH+As_2O_3} CK_2(NO_2)_2 \xrightarrow{H_2SO_4} CH_2(NO_2)_2 \qquad (18)$$

It is unstable at room temperature and is readily decomposed with evolution of nitrogen dioxide. It can be kept for longer periods only at temperature below 0°C or in solution in benzene or some other solvents.

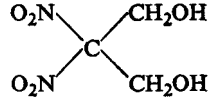
Dinitromethane can exist in two tautomeric forms:



I II

This was based on examination of the ultra-violet and visible spectra (Hedley [44], Hantzsch and Voigt [45]) and electroconductivity measurements (Hantzsch and Veit [46]). The nitro form (I) is colourless, the aci-form (II) is yellow. The aci-form is a relatively strong mono-acid (K_a = 1.43 x 10^{-4} at 0°C and 2.68 x 10^{-4} at 25°C).

Dinitromethane reacts with two mol. of formaldehyde to form the diol (III) [47]



III

Dinitromethane forms salts which are (generally speaking) unstable and decompose at temperatures not very much above 100°C.

TRINITROMETHANE (NITROFORM)

Trinitromethane $CH(NO_2)_3$ forms white crystals (m. p. 25°C). It was first obtained as its ammonium salt by Shishkov [48], by hydrolysis of trinitroacetonitrile with water. It was also Shishkov who obtained trinitroacetonitrile (m. p. 41.5°C) by treating the sodium salt of fulminuric acid with a mixture of nitric and sulphuric acid. Trinitroacetonitrile also exhibits explosive properties.

Baschieri [49] found that nitroform was produced in the reaction of acetylene with anhydrous nitric acid (sp. gr. 1.52). Tetranitromethane, when hydrolysed,

also yields nitroform. Hantzsch and Rinckenberger [50] obtained its ammonium salt by treating tetranitromethane with aqueous ammonia. This method is mostly applied for the laboratory preparation of nitroform.

Nitroform can exist in two forms [50]: a nitro form (I) and an aci-form (II)

$$\underset{\text{I}}{(O_2N)_3CH} \rightleftharpoons \underset{\text{II}}{(O_2N)_2C{=}NOOH}$$

The colourless form (I) exists in solution acidified with hydrochloric or sulphuric acid and also in anhydrous benzene, carbon disulphide and ether. Aqueous and basic solutions are intensely yellow due to the presence of the form II. Solutions in acetic acid are slightly yellow, which would indicate that the two forms exist in equilibrium in this medium.

Most salts derive from the aci-form (II). However, the silver and mercuric salts exist in two forms: colourless and yellow. This would indicate that two forms of these salts - nitro and aci - can exist.

The explosive properties of nitroform have been proved by Shishkov [48]. Nitroform salts also exhibit explosive character.

Trinitromethane reacts with formaldehyde forming trinitroethyl alcohol (Hurd and Starke [51]) :

$$CH(NO_2)_3 + CH_2O \rightarrow C(NO_2)_3.CH_2OH \qquad (19)$$

The reaction is highly exothermic. It should be controlled, so as to prevent its temperature exceeding 70-80°C. Trinitroethyl alcohol is an unstable, crystalline compound, melting at 36-37°C (Ficheroulle and Gay-Lussac [52]). Its initiation temperature is about 120°C.

Trinitroethyl alcohol may be esterified with acetic anhydride to the acetate, which is much more stable than the alcohol itself and at temperatures of 120-140°C shows no distinct signs of decomposition. Both alcohol and acetate are very good solvents for nitrocellulose.

TETRANITROMETHANE

Tetranitromethane was first obtained by Shishkov [48] in 1857, but it was only during the World War II that the Germans experimented with it on a large scale, using mixtures of tetranitromethane with various combustible materials as rocket propellants.

PHYSICAL PROPERTIES

Tetranitromethane, $C(NO_2)_4$, is a heavy oily liquid (sp. gr. 1.65), which solidifies at +3°C and boils at 126°C without decomposition. It is insoluble in water, but it dissolves easily in alcohol and benzene. It is a volatile substance with a characteristic smell, reminiscent of nitrogen oxides.

Menzies [53], later Nicholson [54] and Edwards [551 measured the vapour pressures of tetranitromethane and obtained similar values.

Nicholson found the following vapour pressures for temperatures ranging from 0°C to 40°C:

Temperature, °C	0	13.8	20	30	40
Vapour pressure, mm Hg	1.9	5.7	8.4	14.9	25.8

Changes in the vapour pressure of tetranitromethane depending on temperature may be expressed by a first degree equation:

$$\log p = 8.63\text{-}2260/T$$

From the above data Nicholson has calculated the latent heat of evaporation 10.3 kcal/mole. Edwards has given the following figures for temperatures ranging from 40°C to 100°C

Temperature, °C	40	50	60	70	80	90	100
Vapour pressure, mm Hg	26.5	43.3	68.0	108.0	164.0	239.0	339.6

He has presented changes in vapour pressures as a variable dependent on temperature, according to the equation:

$$\log p = 7.23\text{-}2130/T$$

and has calculated the latent heat of evaporation to be 9.7 kcal/mole.

CHEMICAL PROPERTIES

Although tetranitromethane does not contain active hydrogen it readily enters certain reactions. With water it reacts slowly to form trinitromethane, i.e. nitroform:

$$C(NO_2)_4 + HOH \rightarrow CH(NO_2)_3 + HNO_3 \quad (20)$$

With potassium hydroxide, tetranitromethane readily yields its potassium salt of nitroform :

$$C(NO_2)_4 + 2KOH + CK(NO_2)_3 + KNO_3 + H_2O \quad (21)$$

It react with sodium sulphite to yield sodium trinitromethanesulphonate

$$C(NO_2)_4 + NO_2SO_3 \rightarrow (O_2N)_3CSO_3Na + NaNO_2 \quad (22)$$

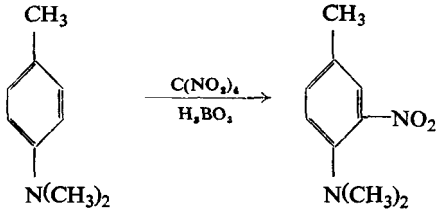
With copper or nickel in the presence of ammonia it forms complex salts having initiating properties (Vol. III).

Tetranitromethane is added to compounds having double bonds to form brown or yellow products. The reaction is very sensitive and may be utilized, for example, for detecting traces of olefins in paraffin fractions (Werner [56]).

Tetranitromethane reacts with tertiary amines, causing their degradation with the formation of N-nitroso derivatives of secondary amines. In this way tertiary amines may be converted to secondary ones (E. Schmidt and co-workers [57, 58]):

$$\begin{array}{l} (R.CH_2)_3N + C(NO_2)_4 \rightarrow (R.CH_2)_2N.NO + R.CHO + CH(NO_2)_3 \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \text{HCl} \qquad\quad \text{OH}^- \\ (RCH_2)_2NH_2Cl: \rightarrow (R.CH_2)_2NH \end{array} \quad (23)$$

Tetranitromethane may be used for nitrations in the presence of boric acid. Dialkylanilines may be nitrated by this method, as for example N,N-dimethyl-p-toluidine (E. Schmidt and H. Fischer [57]):



Tetranitromethane like polynitro-aromatic hydrocarbons is able to form addition compounds (p. 222, Fig. 47). Nevertheless, the existence of an addition compound of tetranitromethane with benzene has not been proved by thermal analysis, when this was carried out recently by T. Urbanski, Piskorz, Centner and Maciejewski [59]. They also examined a number of other systems by means of thermal analysis. The compositions of various eutectics determined by the above authors are shown in Table 127.

TABLE 127

EUTECTICS OF TETRANITROMETHANE

Compound added	Tetranitromethane content, wt. %	Freezing point, °C
Benzene	70.0	-16.1
Nitrobenzene	57.0	-19.1
o- Nitrotoluene	41.5	-28.5
m- Nitrotoluene	47.5	-24.0
p- Nitrotoluene	81.5	+ 1.5
m- Dinitrobenzene	97.0	+11.3
α– Trinitrotoluene	97.0	+12.3
α– Nitronaphthalene	90.0	+ 9.3
Tetryl	(restricted solubility)	-

Macbeth and his co-workers [60, 61] found that tetranitromethane produced yellow or brown colour with a number of other compounds as well, for example, with mercaptans, dioxane, and aliphatic amines. The absorption spectra of such solutions showed maxima at about 350 mμ.

EXPLOSIVE PROPERTIES

According to Roth [62], pure tetranitromethane cannot be detonated even when using 10 g of tetryl as detonator. However, the ability of tetranitromethane to detonate increases considerably when it contains organic impurities, even in small quantities.

Tetranitromethane forms very powerful explosive mixtures with combustible substances, for example with nitrobenzene, and toluene. The explosive properties of such mixtures were investigated in detail after an accidental explosion had occurred in Münster University in 1920.

Naoum [63] gave the following data on the explosive properties of tetranitromethane and of its mixtures. Alone, tetranitromethane gives a lead block expansion of only 40 cm^3 including 8 cm^3 contributed by the detonator.

A mixture of 83.8% of tetranitromethane, 4.9% of toluene and 11.3% of cotton wool gives a lead block expansion of 435 cm^3, i.e. of the order of the most powerful explosive. The above mixture contains a 13% excess of oxygen.

A stoichiometric mixture, with its ingredients taken in such quantities as to have all the oxygen consumed, containing 86% of tetranitromethane and 13.5% of toluene gives an expansion of 465 cm^3.

The density of the mixture is 1.45. According to the Chemisch Technische Reichsanstalt [64] measurements, its rate of detonation is exceptionally high:

in a glass tube of 12 mm diameter 7100 m/sec
in a steel tube of 25 mm diameter 8300-9300 m/sec

Behrens [65] measured the lead block expansions given by tetranitromethane alone or in mixtures with nitrogen dioxide and benzene. Detonators of various strengths from No. 1 to No. 8 were used as initiators. Tests with TNT and nitroglycerine were made for comparison. The results obtained are shown in Table 128.

In another set of experiments Behrens investigated mixtures of tetranitromethane with benzene for their ability to detonate and for explosive power. He found stoichiometric mixtures to be the most powerful.

TABLE 128

No. of detonator	Expansion, cm^3				
	Tetranitromethane	Mixture $C(NO_2)_4$ 70% N_2O_4 30%	Mixture $C(NO_2)_4$ 87% Benzene 13%	TNT	Nitroglycerine
1	12	0	413	0	171
2	44	0	404	0	172
3	65	13	404	218	379
5	86	48	404	268	407
8	71	37	445	332	445

The explosive properties of nitrobenzene-tetranitromethane solutions were examined in detail by Roth [62] who measured rates of detonation power (on a 10.5 by 7 mm crusher gauge), and sensitiveness to impact, using nitroglycerine and TNT as standards (Table 129). Lead block expansions are not included here as they were not determined by standard methods.

TABLE 129

Concentration of nitrobenzene %	Rate of detonation m/sec	Crusher gauge figures mm	Sensitiveness to impact kgm/cm^2
5.0	6870	4.32	4.80
10.0	7030	4.50	4.30
15.0	7480	5.25	4.30
20.0	7550	5.43	3.65
22.5	7700	5.45	5.15
25.0	7575	5.66	8.06
30.0	7500	5.25	8.06
35.0	7220	5.20	15.00
40.0	7000	4.92	15.00
50.0	6700	4.40	no explosion
70.0	5800	3.20	,,
80.0	no detonation	no detonation	,,
Nitroglycerine	7450		4.75
TNT	7200	4.2	11.1

The highest rate of detonation was obtained with a solution containing 22.5% of nitrobenzene, which also proved to be more powerful than nitroglycerine. With regard to sensitiveness to impact, a solution containing 5-10% of nitrobenzene has shown some similarity to nitroglycerine, while that containing 30-40% of nitrobenzene resembled TNT.

T. Urbanski, Piskorz, Maciejewski and Cetner [59] investigated the properties of stoichiometric mixtures of tetranitromethane with benzene and with aromatic nitro compounds. The results obtained are tabulated below (Table 130).

TABLE 130

Composition of the mixture			Density g/cm^3	Rate of detonation† in 20 mm glass tube m/sec	Lead block expansion cm^3
Other component	Concentration wt. %	Tetra-nitromethane concentration wt. %			
Benzene	13.75	86.25	1.47	7180	520
Nitrobenzene	23.15	76.85	1.53	7430	470
o- Nitrotoluene	21.30	78.70	1.52	7770	480
p- Nitrotoluene	21.30	78.70	1.52	8170	495
m- Dinitrobenzene	34.05	65.95	1.53	6670	650
TNT	39.85	60.15	1.58	6670	565
α– Nitronaphthalene	19.70	80.30	1.57	8160	490
Tetryl	51.00	49.00	1.63	7100	570

† For the initiation a No. 8 detonator and 10 g of TNT were applied.

The high, values for the lead block expansion test given by mixtures of tetranitromethane with higher nitrated aromatic compounds are striking. On the other hand, the rates of detonation of these mixture are lower than those of mixtures containing lower nitrated compounds or benzene.

As illustrated by Table 13 1, the sensitiveness to impact of the same mixtures with dinitrobenzene, TNT or tetryl is distinctly higher than that of pure dinitrobenzene, TNT and tetryl.

TABLE 131

Other component	Sensitiveness of the pure component (impact energy) kgm	Sensitiveness to impact of the mixture (impact energy) kgm
m- Dinitrobenzene	19.5	12
α– Trinitrotoluene	12	7
Tetryl	7	3

These mixtures are also more sensitive to flame than nitro compounds alone and can be ignited more readily. A mixture with benzene ignites most readily, hence it can be inferred that ignition is initiated in the gaseous phase.

TOXICITY

Tetranitromethane is highly toxic. Kiese [48] found that 25 mg/per kg of body weight of tetranitromethane slowly injected intravenously caused transitory methaemoglobinaemia, as well as lung oedema and damage to the liver, kidney and central nervous system. Tetranitromethane injected quickly caused necrosis around the puncture which could be fatal.

PREPARATION

Shishkov obtained tetranitromethane by treating nitroform with a mixture of fuming nitric acid with sulphuric acid. Pictet [67] found that tetranitromethane was formed when nitric acid was reacted with acetic acid, or acetyl nitrate with acetic anhydride.

For the preparation of tetranitromethane on the laboratory scale Chattaway's method [68] is commonly used. It consists in treating acetic anhydride with fuming nitric acid at room temperature or below. After a few days the homogeneous solution is poured into water, causing the oily tetranitromethane to separate.

This method was applied in the U.S.A. on a larger scale by Nitroform Products Co., Inc., Newark, N. Y. However, the plant was completely destroyed by an explosion that occurred in the manufacture of tetranitromethane.

Investigation indicated [69] that the probable cause was a rise of temperature in the mixing tank, where nitric acid and acetic anhydride reacted at a temperature

of 15-20°C, maintained by cooling and stirring. The rise of temperature may have been due to breakdown of the stirring equipment. It was also suggested that the presence of iron oxide or some other catalyst may have sensitized the mixture or promoted it to a "wild" side-reaction.

Tetranitromethane may also be obtained by reacting nitric acid with ketene (which may be regarded as a kind of acetic anhydride), according to d'Arsens and G. Levy [70].

Tetranitromethane is also formed during the nitration of aromatic hydrocarbons under very vigorous conditions, for example, when benzene or toluene is nitrated to the trinitro derivative.

MacKie and Orton [71] found that tetranitromethane could be obtained by reacting anhydrous nitric acid with acetylene in the presence of mercuric nitrate. During World War II the Germans manufactured tetranitromethane by this method on a semi-commercial scale, after they had developed the industrial process (Schimmelschmidt [72]).

The reaction takes place in the presence of mercuric nitrate as a catalyst at temperatures ranging from 45°C to 50°C (max. 60°C).

$$CH{=}CH + 2HNO_3 + (NO_2)_2CH\text{-}CHO + H_2O \qquad (24a)$$

$$(NO_2)_2CH\text{-}CHO + HNO_3 \rightarrow (NO_2)_3C\text{-}CHO + H_2O \qquad (24b)$$

$$(NO_2)_3C\text{-}CHO + 2HNO_3 \rightarrow (NO_2)_3C\text{-}COOH + H_2O + 2NO_2 \qquad (24c)$$

$$\downarrow$$

$$(NO_2)_3CH + CO_2$$

$$(NO_2)_3CH + HNO_3 \rightarrow (NO_2)_4C + H_2O \qquad (24d)$$

The overall reaction may be presented as:

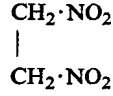
$$C_2H_2 + 6HNO_3 \rightarrow (NO_2)_4C + CO_2 + 4H_2O + 2NO_2 \qquad (25)$$

in addition a side-reaction

$$C_2H_2 + 10HNO_3 \rightarrow 2CO_2 + 6H_2O + 10NO_2 \qquad (26)$$

also takes place.

1,2-DINITROETHANE



m. p. 39°C, b. p. 135°C

1,2-Dinitroethane may be obtained by the action of nitrogen dioxide on ethylene at low temperature (about 0°C) (Semenoff [73]; Demyanov [74], [75]). According to N. Levy, Scaife, Smith [76], the use of a mixture of ethylene with oxygen in the volume ratio of about 4:1 gives good results.

Besides 1,2-dinitroethane a nitrous ester (nitroethyl nitrite) is also formed which is unstable and may decompose. According to N. Levy et ***al.,*** nitroethyl nitrite may be hydrolysed by dissolving the reaction mixture in methyl alcohol. Dinitroethane then precipitates as a crystalline mass.

Nitration is always accompanied by the oxidation of the olefin (Baldock, N. Levy and Scaife [77]).

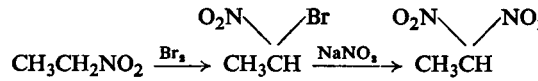
Dinitroethane is a very powerful explosive, giving a lead block expansion of 140-150 (picric acid = 100). Its density is 1.46. It is less sensitive to impact than picric acid. Since it is highly reactive, and hence unstable, it has not found any use as explosive. It reacts most readily with bases. For example, when stored in a glass vessel it decomposes after a few weeks as the result of its contact with glass, which has basic properties. Levy suggests adding to the product an organic acid, as for example *p*- toluenesulphonic acid, as a stabilizer. Under the influence of bases dinitroethane may form nitroethylene, as well as other less defined products, which can readily polymerize to form resinous substances.

1,1-DINITROETHANE

$CH_3CH(NO_2)_2$

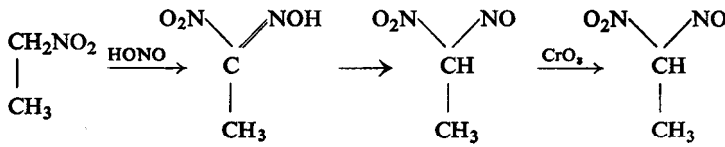
m. p. 37.5°C, b. p. 185°C

This substance was obtained by ter Meer [78] by acting with sodium nitrite on 1-bromo-1-nitroethane:



(27)

It can also be obtained by oxidation of nitrolic acid derived from nitroethane (Topchiyev [79]) :



(28)

Chancel [80a] described another general method of preparing 1,1-dinitroparaffins and in particular 1,1-dinitroethane, starting from ethyl acetoacetate and its derivatives :

$$CH_3COCH(R)COOC_2H_5 \xrightarrow{HNO_3} R\text{-}CH(NO_2)_2 + CH_3COOH + CO_2 + C_2H_5ONO_2$$

The yield of the reaction is relatively low (5-6%).

Recently Novikov [81] prepared 1,1-dinitroethane using this method.

A new excellent method of preparing gem-dinitroparaffins was recently reported by Kaplan and Shechter [97]. It consist in acting with $AgNO_3$ + $NaNO_2$ on sodium salts of nitroparaffins.

This substance has been suggested as monofuel for rocket propulsion (Wood [82]).

POLYNITROETHYLENE

$(CH_2=CHNO_2)_n$

Nitroethylene monomer, $CH_2=CHNO_2$, is a yellowish-green, strongly lachrymatory liquid, boiling at 35°C (at 70 mm Hg). It may be prepared by acting with bases on 1-nitro-2-chloroethane or by the action of potassium hydrogensulphate on 2-nitroethyl alcohol (Wieland and Sakellarios [83]). Very satisfactory results may be obtained with phthalic anhydride as dehydrating agent (Buckley and Scaife [84]; Boileau and Runavot [85]; Sokolov, Perekalin et al. [98]).

It can also be obtained by acting with urea on 1,2-dinitroethane:

$$\begin{array}{l} CH_2NO_2 \\ | \\ CH_2NO_2 \end{array} \xrightarrow{CO(NH_2)_2} \begin{array}{l} CHNO_2 \\ \| \\ CH_2 \end{array} + HNO_2 \qquad (29)$$

Nitrous acid then reacts with an excess of urea in the usual way.

Nitroethylene readily polymerizes to yield a white powder, insoluble in water and in most organic solvents. It may be obtained by direct action of bases on nitroethyl nitrate or -acetate or on dinitroethane.

Polynitroethylene burns without melting. It is a very weak explosive, which gives a lead block test amounting to about 30% of that given by TNT. It has not found any practical uses because of its low thermal stability.

A number of other nitro-olefins can be prepared in a similar way as nitroethylene [86].

SYM-TETRANITROETHANE

This compound is known in the form of the potassium salt $C(NO_2)_2KC(NO_2)_2K$. Its preparation and use in the production of hexanitroethane is discussed below.

HEXANITROETHANE

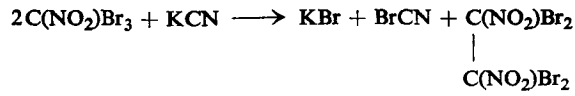
$$\begin{array}{l} C(NO_2)_3 \\ | \\ C(NO_2)_3 \end{array}$$

m. p. 142°C

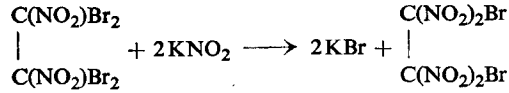
The product is known as a colourless crystalline, rather non-volatile substance, having explosive properties, It was first obtained by Will [87] when acting with nitric acid on potassium salt of tetranitroethane:

$$C_2(NO_2)_4K_2 + 4HNO_3 \rightarrow C_2(NO_2)_6 + 2KNO_3 + 2H_2O \qquad (30)$$

For the preparation of the latter, Will applied Scholl's method [88], consisting in reacting potassium cyanide and nitrite with bromopicrin, according to the reactions :



(31a)

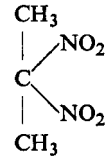


(31b)

(31c)

Hexanitroethane gives a lead block expansion of 180 cm^3. It is more difficult to explode by impact than picric acid. With TNT or tetryl (in stoichiometric ratio) it forms exceptionally powerful explosives. Since it has the ability of gelatinizing nitrocellulose the Köln-Rottweil powder factory [89] tried to use it as a smokeless powder component to increase the explosive power of the latter. However, because of the high production costs of hexanitroethane, it has not found a practical use. In addition, its chemical stability is rather low: when heated it begins to decompose at 75°C.

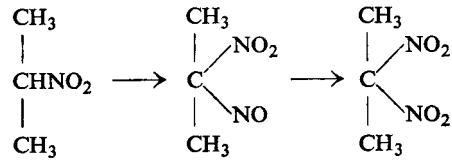
2,2-DINITROPROPANE



m. p. 51-52°C

2,2-Dinitropropane forms white crystals, insoluble in water.

It is usually obtained by oxidizing pseudonitrole formed from secondary nitropropane (Born [go]), Denton ***et al.*** [99].



(32)

2,2-Dinitropropane exhibits strong explosive properties. The initiation temperature, with an induction period of 5 sec is 360°C. Its sensitiveness to impact is of the order of TNT. The explosive power of dinitropropane is higher than that of TNT: it amounts to about 120, compared with 100 for TNT.

2,2-Dinitropropane has the disadvantage of being highly volatile: when stored in a vessel that is not quite tight at 75°C for 48 hr it loses about two thirds of its volume.

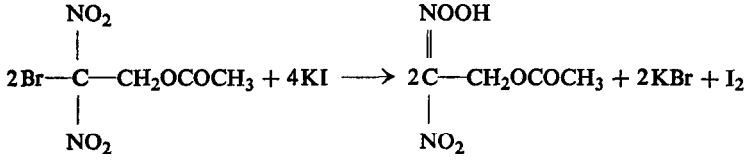
2,2-Dinitropropane has been suggested (Albright, Nelson and Raymond [91]) as an additive for Diesel engine oil to increase its octane number. With a 0.1%

content of dinitropropane the octane number of the fuel increases from 44 to 51, while with 0.5% it increases to 53.5.

OTHER POLYNITRO ALIPHATIC COMPOUNDS

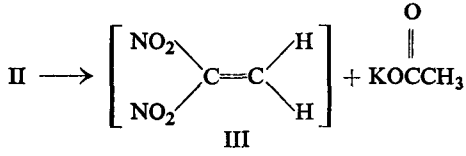
A new general method of preparing polynitro aliphatic compounds was recently described by Frankel [92]. The reaction consists in acting with 2-bromo-2,2-dinitroethyl acetate (I) on metallic salts of organic and inorganic compounds having active hydrogen atoms.

The following mechanism is given by the author, for the formation of 2,2,4,4-tetranitrobutyl acetate (V) :



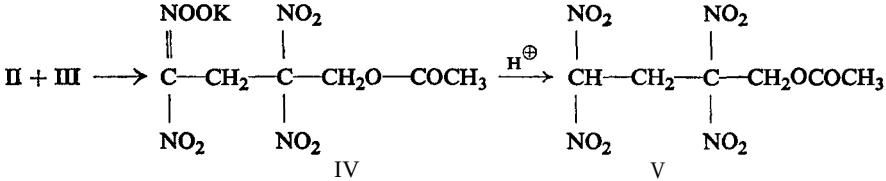
(33a)

I II



(33b)

III



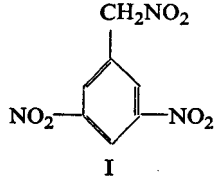
(34)

IV V

It is suggested that the reaction occurs through the intermediate formation of 1,1-dinitroethylene (III). The reaction was described as “dinitroethylation”.

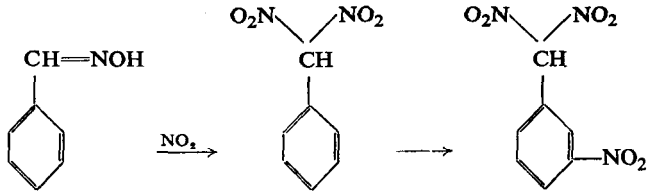
NITROAROMATIC DERIVATIVES OF MONO-, DI-, AND TRI-NITROMETHANE

T. Urbanski and Gedroyc [93] prepared dinitrophenylnitromethane (I) - a trinitrotoluene isomer - by nitration of phenylnitromethane. The compound has proved to have explosive properties similar to those of TNT.



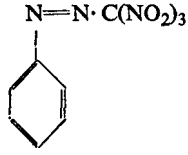
I

Milone and Massa [94] prepared another isomer of trinitrotoluene, namely nitrophenyl dinitromethane (II) by the action of nitrogen dioxide on benzaldoxime followed by the nitration of the resultant product:



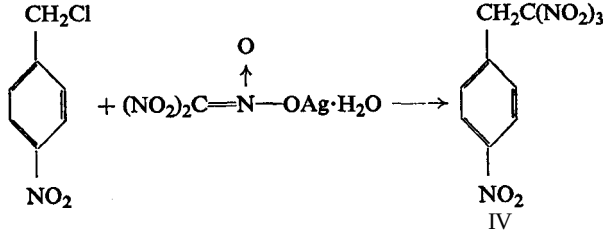
(35)

Ponzio [95] obtained unstable aromatic azo derivatives of trinitromethane (of the type III) by reacting the ammonium salt of trinitromethane with diazonium salts:



III

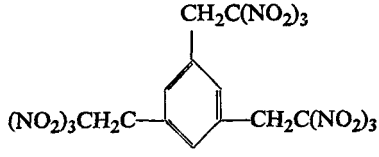
W. S. Reich [96] prepared aromatic derivatives of trinitromethane (of the type IV) by acting with the silver salt of nitroform on ar-alkyl chlorides, as for example *p*- nitrobenzyl chloride :



(36)

IV

In a similar way he obtained compound V from w,w',w"-triiodomesitylene:



V

Compounds of this type are powerful explosives.

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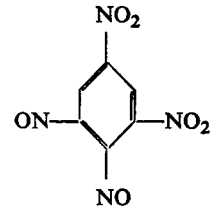
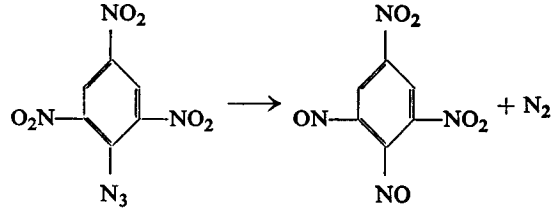
CHAPTER XX

NITRONITROSO AND NITROSO COMPOUNDS

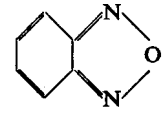
DINITRODINITROSOBENZENE



THE METHOD of the preparation of dinitrodinitrosobenzene has already been discussed (see p. 263). This product also forms in the thermal decomposition of picryl azide at temperatures of 90-100°C. In addition, nitrogen is generated in the reaction (Rathsburg [I]):



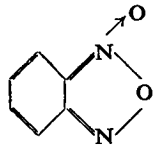
More recent studies on the structure of *o*- dinitroso derivatives of benzene indicate they may have the benzofurazan ring (I) which was described for the first time by Forster and Fierz [2].



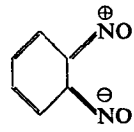
I

Green and Rowe [3] suggested a benzofuroxane structure (II) for *o*- dinitrosobenzene and its derivatives. This view was further developed by Hammick,

Edwards and Steiner [4] and also by Gaughran, Picard and Kaufman [5]. However, Boyer expressed the view that the *o*- dinitroso structure (III) is more probable:

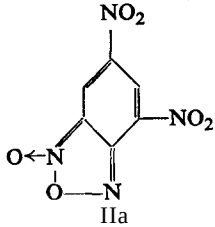


II

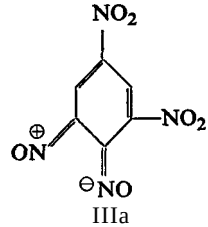


III

In the light of the above, the structure of dinitrodinitrosobenzene should be presented by the formulae IIa and IIIa respectively:



IIa

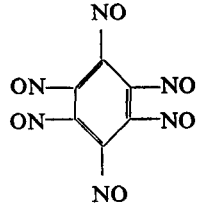


IIIa

In the end the benzofuroxane structure (II) was accepted for *o*- dinitrosobenzene (mainly on the basis of the NMR spectrum (Engler [7]).

Dinitrodinitrosobenzene is a powerful explosive: it gives a lead block expansion of 360 cm^3.

HEXANITROSOBENZENE

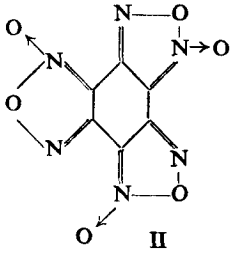


I

By heating trinitrotriazidebenzene (see Vol. III) at 100°C or higher Turek [8] obtained a compound to which he assigned the structure of hexanitrosobenzene (I, m. p. 159°C).

Hexanitrosobenzene is a stable, non-hygroscopic substance. It is more sensitive to impact than tetryl. The lead block expansion it gives is larger than that given by tetryl.

In the light of the above considerations the benzotrifuroxane structure (II) might be assigned to the Turek's hexanitrosobenzene,



II

Nitrosophenols have already been dealt with in the chapter on nitrophenols.

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